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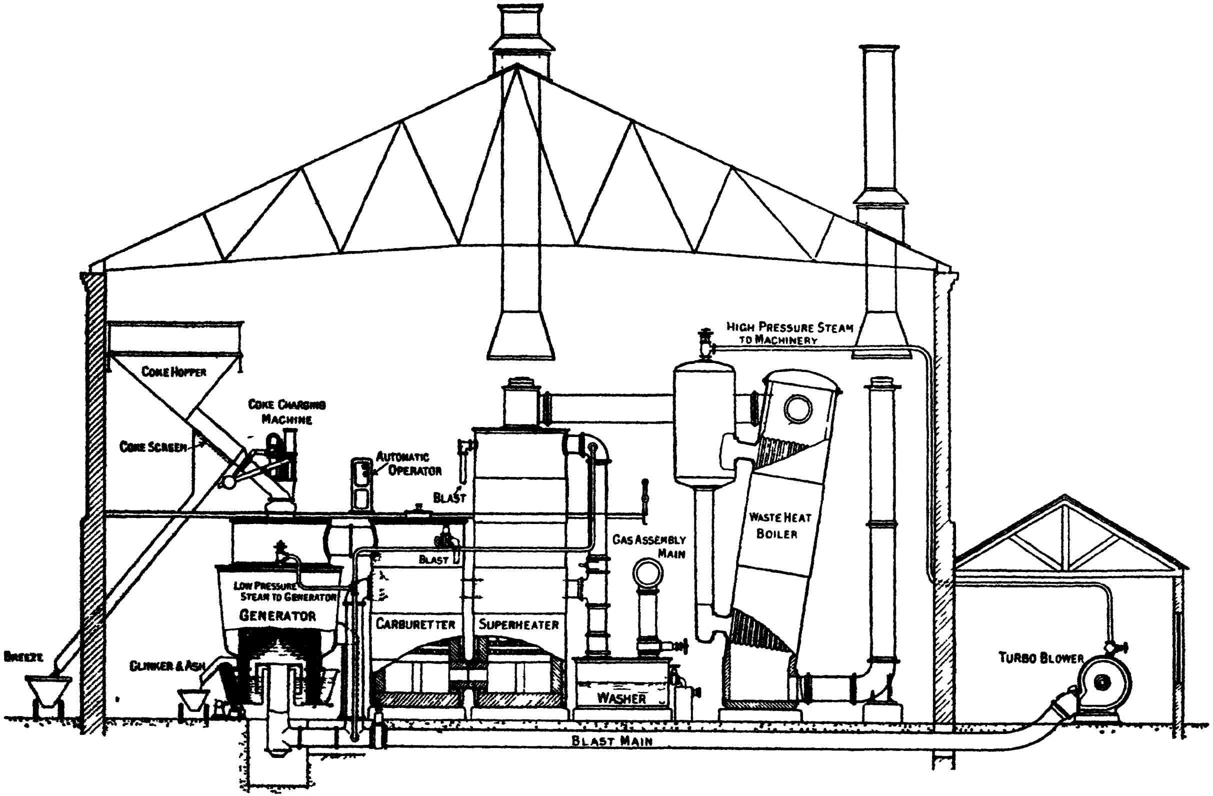

Carburetted Water-Gas Plant. Humphreys and Glasgow System.

[*Frontispiece.*

FUEL

SOLID, LIQUID AND GASEOUS

BY

J. S. S. BRAME, C.B.E., F.I.C., F.C.S.

AND

J. G. KING, Ph.D., A.R.T.C., F.I.C.

FOURTH EDITION

LONDON
EDWARD ARNOLD & CO.

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First Published 1914
Second Edition 1917, Reprinted 1919, 1920
Third Edition 1924
Fourth Edition 1935, Reprinted 1939, 1942

**PRINTED BY THE REPLIKA PROCESS
IN GREAT BRITAIN BY
LUND HUMPHRIES
LONDON · BRADFORD**

PREFATORY NOTE

For the extensive revision demanded to bring this Edition thoroughly up to date, so much progress having been made in the ten years since the Third Edition was published, I felt it was desirable to have the collaboration of one who had been closely associated and in constant touch with the researches and developments in the technology of Fuel. I was fortunate in finding in Dr. J. G. King a willing collaborator and joint Author. To him my grateful thanks are due.

J. S. S. B.

PREFACE

This Fourth Edition is really the coming-of-age edition of Fuel, which was first published in 1914. During the years which have elapsed since the Third Edition was issued, there have been so many developments in the technology of fuel, some entirely novel, like hydrogenation, and so much active research work, as for example that carried out at the Fuel Research Station, Greenwich, that a very complete revision was imperative.

Coal has naturally continued to inspire the investigations of the laboratory and its utilization those of the technician. The organized investigation of our British coal measures, advocated as so necessary in the First Edition, has been placed on a firm basis and already has yielded valuable data, since it is characterized by reliability, which could hardly be claimed for much of the earlier data on British coals.

Although these investigations must go on for many years, the material already available has enabled us to give much more detailed information, and the whole of the Chapters dealing with coal have been completely re-written.

In the utilization of coal, particularly its combustion in the pulverized form, considerable extension has been possible. Coke, again, has been the subject of much research particularly as regards the evaluation of its properties. The preparation of coal for the market has engaged the attention of technologists, and the more important underlying principles and technique are dealt with.

Hydrogenation of coal (and to a lesser extent of tar and tar oils) has been very much in public evidence of very recent years, and even the layman has been impressed by its possibilities as a British source of liquid fuels, particularly petrol. The inclusion of reliable data on the process and the character and yield of the products is therefore an important addition to former editions.

No section of full technology has been the subject of more research than that of fuels for internal combustion engines, particularly since the marked success of the high-speed compression-ignition engine ("Diesel" engine). The information regarding these fuels has been thoroughly revised, but both in this country and in the United States of America much activity in researches on high-speed engine fuels is in progress.

There has been a considerable change in the economic position of the poorer gaseous fuels—producer gas—largely owing to the development of the heavy oil engine and electric power distribution. Whilst the principles underlying their production has required little alteration, considerable reduction in space has been possible in other directions. Water gas, and particularly carburetted water gas, because of the much wider use of the latter in the Coal Gas industry, have required more adequate treatment.

In the Section on Fuel Analysis and Calorimetry, the work of the Committees of the B.S.I. and I.P.T. in standardizing methods of sampling and analysis has been an important development in Fuel Technology. The methods, being readily available in the publications of these bodies, have not been dealt with in detail, but it is hoped that sufficient information has been included to indicate the most suitable methods and the precautions which must be observed in employing them. Special reference should perhaps be made to new material dealing with Recording Gas Calorimeters, instruments of great importance, since the basis of valuation of gas has been changed from cubic measurement to a calorific standard.

J. S. S. B.
J. G. K.

ACKNOWLEDGEMENTS

The Authors wish to acknowledge the help given by Mr. H. J. Orton for the preparation of drawings from which several new blocks have been prepared, and Mr. E. C. Evans for information on the utilization of Blast Furnace Gas.

In particular their thanks are due to the Controller of His Majesty's Stationery Office for according permission for the reproduction of the illustrations below, these being Crown Copyright:

Fig. 11. Fuel Research Station Grid burner for pulverized coal.
,, 12. Apparatus for the Determination of the Reactivity of Coke.
,, 18, 19. Apparatus for Measurement of Radiation from Fires.
,, 45. Fuel Research Station Industrial Gas Burner.
,, 67. The Gray-King Low Temperature Assay Apparatus.

Acknowledgment and thanks are also due to the following for material, for loan of blocks or diagrams, etc., from which blocks have been prepared:

A.E.G.	Ranarex CO_2 instrument.
Babcock & Wilcox, Ltd.	Pulverized coal plant.
Baird & Tatlock, Ltd.	Bomb calorimeters,
Brayshaw Furnaces & Tools, Ltd.	Gas furnace.
Brett Patent Lifter Co., Ltd.	Fuel oil and burner furnace.
Cambridge Instrument Co., Ltd.	Gas calorimeter. CO_2 recorder.
Combustions Ltd.	Fuel oil burner.
Dr. D. T. Davies	Coal-washing plant.
Humphreys & Glasgow, Ltd.	Water gas plant. "Complete gasification" plant for coal.
Imperial Chemical Industries, Ltd.	Coal hydrogenation plant.
International Combustions Ltd.	Morgan gas producer.
J. Samuel White & Co., Ltd.	Fuel oil burners.
Kermode Ltd. (Liverpool)	Fuel oil furnace front.
Koppers Coke Oven Co., Ltd.	Coke oven. Gas producer.
Morgan Crucible Co., Ltd.	Fuel oil burner. Melting furnace.
National Petroleum News	Hydrogenation plant for tar.
Power Gas Corporation, Ltd.	Water gas and carburetted water gas plant.

Urquharts (1926), Ltd.	Fuel oil burners.
Wallsend Slipway & Engineering Co., Ltd.	Fuel oil burners.
Woodall-Duckham Vertical Retort & Oven Construction Co., Ltd.	Coke oven (Semet Solway).

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FUEL—SOLID, LIQUID AND GASEOUS

PART I

SOLID FUELS

CHAPTER I

INTRODUCTION

With the exception of natural oils, the origin of which still remains uncertain, all forms of fuel may be regarded as derived primarily from cellulose, often associated with materials of a gum or resin character. During the life of a plant the green colouring matter of the leaves has the power, under the influence of sunlight, of causing combination between the carbon dioxide of the air and the water in the plant to produce ultimately the cellulose, which is the main constituent of woody fibre, returning to the air the oxygen previously associated with the carbon dioxide. The wonderful mechanism by which these vital changes are brought about is quite unknown, but the final result is threefold—the amount of carbon dioxide in the atmosphere is prevented from becoming excessive, which would be fatal to animal life, the renewal of the oxygen supplies is assured, and, what is of special importance since the change involves the absorption of radiant energy from the sun, available heat is stored up by the plant, which may be utilized afterwards by man for the thousand and one purposes for which he requires fuel.

Cellulose, in the form of wood; peat, where the cellulose has undergone some slight metamorphosis; lignite, brown coal, and finally, all the various kinds of coal, from highly bituminous to anthracite, certainly have derived their heat energy by this process, and whether we employ these cellulose derivatives in their natural form or convert them into forms more suitable than the original for special purposes, such as charcoal and coke, or employ them as liquids (tar) and gases, as is now such general practice, we are but recovering this energy stored up from the sun.

For a solid substance to be of value as a fuel it must fulfil the conditions of igniting with comparative ease, burning freely in some cases with a long flame, in others without flame, and possessing as high a calorific value as possible. From the economical point of view regular supplies must be available, and the cost sufficiently low.

Generally the proportion of hydrogen present is the determining factor in the ignition point of a fuel, this being well illustrated in the case of charcoal, which, if carbonized below a visible red heat (340° C. ; 644° F.) ignites at 800° F., whilst if carbonized at a bright red heat (900° C. ; 1634° F.) it ignites at approximately 1000° F.

The burning character will be dependent largely upon the draught conditions, i.e. the rapidity with which air is supplied to the fuel, and frequently for perfect combustion on the temperature of this air. For flame to be formed a solid fuel must give off a quantity of combustible gas, in which case combustion is spread over a large area and high intensity is not attained. For this latter effect a solid fuel evolving little or no gas, but burning completely and rapidly on the fire bars or in direct contact with the material to be heated is requisite.

With liquid fuels, used in internal combustion engines, the ignition temperature is of great practical importance. In compression/ignition engines firing of the oil charge (especially with a cold start) is determined by the ignition temperature. In engines where the fuel/air mixture is compressed before being fired by a spark, or other method, the limit of compression permissible without risk of pre-ignition is obviously determined by the ignition temperature of the mixture. Further, the question of liability to detonation is closely associated.

The calorific value is dependent upon the elements present in the fuel which are capable of undergoing oxidation with the production of heat, and for all practical purposes two elements only need be considered—carbon and hydrogen. If a fuel contains only these elements its calorific value will be the sum of their heat energies less any heat required to render them available for oxidation. Their ratio is important since the calorific value of hydrogen is 62,100 B.Th.U. (gross) and of carbon, 14,630 B.Th.U. per lb. A high hydrogen/carbon ratio is therefore advantageous.

In most fuels, however, a certain proportion of oxygen is already present, so that the hydrogen and possibly the carbon to some extent are already in combination with oxygen. The nature of this combination is not known, but it is customary to assume that the oxygen is associated wholly with the hydrogen, the balance being referred to as *available hydrogen.* In no substance used as a fuel is the amount of oxygen present more than sufficient to satisfy the hydrogen. It follows, therefore, that oxygen-containing fuels become proportionately poorer fuels as the percentage of oxygen increases.

In considering the value of fuels from the economic point of view, choice is limited to a large extent by proximity of supplies of a certain type, since freight charges are diminished and interruption of supply is less likely to occur. At one time, for example, imported patent fuel (coal) from South Wales was the staple fuel on the Mexican railways, but with the discovery of oil-fields in Mexico it has naturally been superseded by oil fuel. Similarly, wood has been displaced by oil on many foreign railways. Given alternative supplies of fuel of a certain suitable kind the choice should be governed largely by the heat units available per unit of cost, or the purchase arranged on a basis of payment for actual heat units delivered, a matter that is slowly receiving the attention which its importance merits.

Again it may be economical to prepare a fuel, possibly of more suitable character, by the pre-treatment of a raw fuel, as, for example, the carbonization of wood and coal to produce charcoal and coke respectively, at the same time producing valuable by-products such as the tars and gases, or even converting coal into " oils " and motor spirit.

Before proceeding to a consideration of the various forms of fuel there are certain important matters relating to its combustion generally, which must be dealt with briefly.

Combustion. As usually understood, combustion or burning of all commercial fuels is associated with chemical changes brought about by combination of the combustible constituents of the fuel with the oxygen of the air, the reaction developing heat and being easily manifest to the senses. Such a process is termed " rapid combustion," but similar changes may take place at a much slower velocity; the heat developed per unit weight of fuel is the same, but owing to the slowness of its production and its dissipation it is not always apparent. Such a process is termed " slow combustion."

For the desired chemical changes to be complete in order that the whole of the heat units in the fuel may be utilized there must be no insufficiency of oxygen (or air), and from the composition of any fuel the theoretical amount of air requisite may be calculated, as is shown later. Incomplete combustion, resulting not only in losses of heat units through causes apparent to the eye, such as smoke, may also be present and escape observation, and can be detected only by chemical analysis of the flue gases. A common case is the production of carbon monoxide by the incomplete combustion of the carbon of a fuel, which may occur under some conditions of boiler firing, or in the cylinders of internal combustion engines—notably when using petrol.

Incomplete combustion may be avoided only by proper attention to the supply of sufficient air; the intimate contact of the air with the fuel, either at its surface or by thorough admixture with the gases and vapours first evolved; lastly, by ensuring that there is no cooling *of the system to a temperature below that necessary for the reactions* to become complete. Smoke is the visible indication of incomplete combustion, and the above principles lie at the root of its prevention.

Production of Flame. Flame is produced by the combustion of gases and vapours, in the case of solid fuels these being volatilized by heat from the fuel, or by the incomplete combustion of the carbon which gives rise to carbon monoxide, an inflammable gas. The temperature resulting from the combustion must be sufficiently high to maintain the reaction, otherwise the flame is extinguished. In the case of solid fuels, like coal, the amount of flame produced will be dependent largely on the ratio between the volatile combustible constituents and the carbon residue, which is non-volatile. It will be seen later that this ratio is highest with bituminous coals and falls to a minimum with anthracite.

When flame is produced, the heat units from the fuel are generated throughout probably several cubic feet of space. High local intensity with such fuels cannot be attained. When this is desired combustion must take place as far as possible on the grate, so that a fuel low in volatile constituents, such as anthracite, coke, or charcoal must be employed.

In general, flame is inefficient for heating purposes where there is a great difference between its temperature and that of the surface being heated, as in a boiler. This is due to two causes, the checking of combustion by lowering of temperature, and the formation of a thin layer of gas, which is a poor conductor of heat, along the surface of the plate. Much depends, however, on the luminosity of the flame. Owing to the presence of highly heated particles of solid carbon, to which most of the luminosity of all ordinary flames is due, the radiant effect from such flames is fairly high, whilst with a non-luminous flame radiation is much less.

Ignition Point. For active combustion to be initiated a definite temperature must be attained, and for its continuance this temperature at least must be maintained. The ignition point of all combustible substances is no doubt at a fixed temperature, but many conditions influence the ease with which combustion may be started, mass and fineness of division being the most important. Whilst a given coal in a finely divided condition will ignite at a low temperature, a lump of the same coal will require considerable heating up before it takes fire, due to the smaller surface exposed to the air in proportion to mass, which carries away the heat.

The ignition point of solid and liquid fuels is very difficult to determine, because so much depends upon the conditions of the experiment. Coal, for example, quickly yields smoke, vapours and gases, and with slow heating up the ignition point found is really that of the semi-coked residue. No pretension will therefore be made to give exact figures for the ignition points of various coals; at present they depend too much upon conditions to be quoted numerically. It may be stated, however, in general terms that the ignition point falls more or less progressively from anthracites to lignites.

F. S. Sinnatt and B. Moore (*J.S.C.I.*, 1920, **39**, 72 T.) have used an adaptation of H. Moore's crucible method (see below) for ascertaining the ignition point of coals in oxygen. These authors employed from 5 to 6 mgm. of the finely powdered coal (usually passing a 200 I.M.M. sieve), and noted particularly the temperature and time interval before (1) the commencement of visible active combustion, i.e. the mass glowed; (2) ignition, as manifested by an explosion or the production of flame. The time interval was, of course, lessened as the temperature increased, and the authors take a time limit of four minutes and regard the ignition point as the lowest temperature which will cause the fuel to glow or ignite in this time. Such an interval seems excessive, for it is inconceivable that the few milligrams of coal used were not raised to the temperature of the crucible in a very few seconds; and during such prolonged heating as four minutes in oxygen considerable chemical action is most likely to have occurred.

A summary of Sinnatt and Moore's results are given in Table I, and also the " glow " temperature (at which undoubtedly active combustion has commenced) for a heating period of approximately ten seconds. In the author's opinion these latter figures, although based on a somewhat arbitrary standard, more truly represent the ignition point, and from the temperature/time curves given in the original paper, the ignition temperature begins to assume a fairly constant value after about ten seconds' heating, except in the case of anthracite.

That surface action plays an important part in determining the temperature at which active combustion starts is shown by the much higher temperatures for coal passing a 100 I.M.M. sieve, as is shown by the following results:

	Ignition temperature °C.	
	Passing 200 mesh.	100–200 mesh.
Indian coal	240	Above 380
Hoo cannel	229	,, 390
Yard coal	219	,, 396
Gob fire coal No. 1	232	346
Gob fire coal No. 2	225	298

It should be noted that ignition temperatures are always much lower in oxygen than in air, so that considerably higher figures would have been obtained if the atmosphere had been air instead of oxygen. In air the ignition temperatures of coals are of the approximate order: bituminous gas coal, 370° C.; ordinary bituminous coal, 400–425°; Welsh steam coal, 470°; anthracite, 500° C.

TABLE I

SPONTANEOUS IGNITION TEMPERATURE OF SOLID FUELS IN OXYGEN

(F. S. Sinnatt and B. Moore)

	Glow.		Ignition.		Glow temperature for 10 seconds' heating.
	°C.	Seconds.	°C.	Seconds.[1]	°C.
Anthracite	250	45	258	61	340
Hoo cannel	225	33	230	—	334–343
Wigan Arley coal . .	181	70	188	230	272–296
Wigan Yard coal . .	219	17	219	52	270
Gob fire coal No. 1 .	228	29	228	64	278–300
Gob fire coal No. 2 .	228	25	228	55	265–290
Wood charcoal . . .	248	—	248	—	—
Irish peat	300	—	300	—	—
Cellulose	324	—	324	—	—

[1] Includes the time for glow also.

K. Bunte and A. Kölmel give the following ignition points for carbonized fuels: wood charcoal, 252° C.; semi-coke (i.e. produced by low-temperature carbonization), 395° C.; gasworks coke, 505° C.; coke-oven coke, 640° C., but, as shown by E. R. Sutcliffe and E. C. Evans (p. 141), porosity has a very great influence on this. The uncertainty of ignition temperature data is evidenced by the fact that one of the authors has found that the figure for semi-coke may be as low as 220° C.

In the case of highly volatile spirits and of gases the ignition point of the mixture with air, as employed in internal combustion engines, is, however, of great importance, since on this the question of the detonation and pre-ignition of the charge on compression is chiefly dependent, and the degree to which compression of the charge may be safely carried.

H. Moore (*J.S.C.I.*, 1917, **36**, 109; also *J. Inst. Pet. Tech.*, 1920) determined ignition points for liquid fuels by allowing the fuel to fall drop by drop into a crucible heated in a special metal container, and H. Ricardo (*Automobile Engineer*, 1921) and H. B. Dixon (*J.C.S.*, 1911, **99**, 589) have used adiabatic compression of vapours with air. The results with compression by the two observers are widely different in some cases. Unfortunately, there are few instances where comparison is possible between the drop method of Moore with air and the compression method. In the case of benzene, however, the results, both by Ricardo and Dixon, are very much lower than by Moore's drop method, and the same remark applies to toluene. From the table on p. 7 it will be seen that ignition temperatures in oxygen by Moore's method are very much lower than in air. Without claiming any great accuracy for the adiabatic-compression method, the results certainly are more likely to be of practical service, because compression usually occurs in practice, and the atmosphere is air and not oxygen.

Spontaneous ignition temperatures determined with pure oxygen are sometimes claimed as being more in accordance with practice in the compression/ignition engine since the oxygen concentration is nearer that of pure oxygen when the air mixture is under compression, but the fact that the nitrogen is equally compressed and that this inert gas is interspersed with the oxygen cannot but raise doubts on the validity of such a claim.

TABLE II

Spontaneous Ignition Temperatures of Hydrocarbons, etc. (°C.)

	By drop method in hot crucible. (Moore.)		By adiabatic compression with air.	
			(Ricardo.)	(Dixon.)
	In oxygen.	In air.		
Petrols	270–280	360–390	353–367	—
Pentane	—	—	—	510 (40·0)
Hexane	287	—	366	500 (47·5)
Heptane	281	—	330	—
Benzene	566[1] 620[2]	—	419	464 (37·5)
Toluene	516[3] 596[4]	—	422	—
Alcohol, ethyl	395	518	514	550 (15·0)
Ether, ethyl	190	347	256	315–325
Alcohol, 6 vols., and ether, 4 vols.	—	—	—	370 (21·0)
Kerosine	250	367–432	—	—
Tar oil	465	—	—	—
Coal- and coke-oven tars	445–495	—	—	—

[1] 100 per cent. [2] "Crystallizable." [3] 90 per cent. [4] "Pure."

Figures in brackets to Dixon's results give volumes of air to one volume of vapour.

W. R. Ormandy and E. C. Craven (*J. Inst. Pet. Techs.*, 1924, **10**, 335) have made a further study of the spontaneous ignition temperature of volatile fuels, using a modification of Moore's apparatus, which enabled a variation in the size of the chamber to be made. With pure heptane these authors obtained a value of 245° C., which was 36° below Moore's figure, and they concluded that the chief cause of the difference lay in the form and volume of the chamber. Variation in the supply of oxygen had little effect with heptane, but the results show how important conditions are and how difficult it is to obtain an absolute value for ignition temperatures.

The following ignition temperatures for petrols are given:

Pratt's No. 1 . .	285° C.	Shale	278° C.
"B.P."	279° C.	Kerosine . . .	257° C.
Shell	284° C.		

Many factors influence the results of determinations of the S.I.T. of liquid fuels, e.g. in the "drop" method the nature of the surface on which the liquid falls; the volume of the chamber; the pressure and time lag. N. J. Thompson (*J.I.E.C.*, 1929, **21**, 134) gives results for hydro-carbons and alcohols in pyrex glass vessels and copper, steel and chromium-plated cylinders. Bridgeman and Marvin (*loc. cit.*, 1928, **20**, 1219) and Masson and Hamilton (*loc. cit.*, 1927, **19**, 1335) have investigated these various factors.

Increased pressure lowers the S.I.T. of vapours and gases. Tausz and Schutte found a gasoline which ignited at 350° at 2·5 atmospheres ignited at 232° C. when the pressure was 10 atmospheres.

The ideal method would be determination in air under the pressure and temperature conditions of practice, especially in the case of fuels for compression/ignition (C.I.) engines. One or two fuels were examined under these conditions by Hawkes in the Admiralty Engineering Laboratory, but the appliances were only possible in a large engineering laboratory. A valuable symposium on S.I.T. was presented before the Institution of Petroleum Technologists (*J. Inst. Pet. Tech.*, 1932, **18**, 533–94) and F. A. Foord described the apparatus developed at the Royal Air Force Establishment, Farnborough.

Foord points out the importance of time lag between injection and actual ignition and the above apparatus records this electrically. Usually the S.I.T. is taken as the lowest temperature at which the fuel, after an infinite delay, will ignite—this may amount to seconds and clearly the "wait" period is important. Naturally it is reduced by rise of temperature, and the period should not be more than one- or two-fifths of a second.

From curves given by Foord the following delay times and ignition temperatures (in air) have been deduced:

Seconds.	3	2	1	$\frac{1}{5}$
Gas oil . . . . (mainly paraffin)	340° C.	350° C.	375° C.	500° C.
Diesel oil . . . . (mainly naphthene)	390	412	450	575
Creosote	485	505	533	620

Townend and Mandekar (*Proc. Roy. Soc.*, 1933, A, **141**, 484) record that, under certain conditions of pressure, the S.I.T. of butane/air mixtures fall into two more or less well-defined and widely separated temperature ranges, and Coffey and Birchall (*Chem. and Ind.*, 1934, **53**, 245) describe how, with a modified Moore apparatus, a standard petrol gave two fairly well-defined ignition temperatures. For example, a lower range of 320–335° C., then on raising the temperature further no ignition occurred until 420° C. (and above) was reached. An important observation was that the addition of anti-knocks narrowed down the lower zone until it finally disappeared. Similar observations had been made by Prettre (1932).

Townend and Cohen (*Chem. and Ind.*, 1934, **53**, 267) discriminate between the two as (*a*) due to "cool" flames (first noted by W. H. Perkin in 1882) and (*b*) true ignition, and state that *true* ignition in the lower temperature range with hydrocarbon/air mixtures is comparatively rare at atmospheric pressures, but with petrol/air mixtures at 1·9 atmospheres ignition was possible at all temperatures above 284° C., from which it was deduced that "knock in an engine was related to a compression ratio adequate to allow spontaneous *true* ignition in the lower temperature range, which lies within the ordinary working temperatures of petrol/air engines."

The ignition temperature of a gaseous mixture is not constant but varies to some extent with concentration. Near the limiting proportion, however, variation of the proportions of gas and air does not affect the ignition temperature. Values are determined by mixing pre-heated streams of gas and air or oxygen, the values obtained with oxygen being generally the lower. Values for the more important gases are given by Dixon and Coward as:

IGNITION TEMPERATURES OF GASEOUS MIXTURES IN °C. AT ORDINARY PRESSURES

Gas.	In oxygen.	In air
Hydrogen	580–590°	580–590°
Carbon monoxide . . .	637–658	644–658
Methane	556–700	650–750
Ethane	520–630	520–630
Ethylene	500–519	542–547
Acetylene	400–440	406–440

It will be noted that, whilst in the case of simple gases like hydrogen and carbon monoxide the ignition temperature variation is small, in the case of hydrocarbon gases the temperature is uncertain to over 100° C. Further, whilst there is close agreement between the values in oxygen and air in some cases, in other cases there is a marked discrepancy. Ignition temperature is lowered by increase of pressure, a factor of importance in the gas engine.

Theoretical Air for Combustion. This is a most important consideration, governing to a large extent the arrangements for the supply of air, especially in internal combustion engines, and, further, enabling the theoretical composition of the flue or exhaust gases to be determined, which, as will be dealt with fully later, has an important bearing on fuel economy.

Custom has established somewhat firmly the calculation of the air required in pounds, and weight units do not involve corrections for temperature, but since gases are measured in cubic feet and thought of in terms of volumes and not weight, it seems more reasonable to consider their consumption in such units. In either case the calculation is simple, being based on the known combining values of oxygen with the individual combustible constituents, using their ordinary expression in the form of chemical equations for convenience.

The following data are of great service in such calculations, since they apply to all cases of chemical combination where gases are involved.

	At 0° C. and 760 mm. pressure.	At 60° F. and 30 inches pressure.
The molecular weight in grams always . .	= 22·32 litres	23·52 litres
The molecular weight in ounces always . .	= ,, cubic ft.	,, cubic ft.
The molecular weight in pounds always . .	= 357·5 cubic ft.	377 cubic ft.

Conversely, the weight of 1 cubic foot in pounds will equal $\frac{\text{molecular weight}}{357\cdot5}$ at 0° C. and 760 mm., and $\frac{\text{molecular weight}}{377}$ at 60° F. and 30 inches.

Further, the composition of air is :

	By weight.			By volume.		
	Per cent.	Ratio N/O	Ratio air/O	Per cent.	Ratio N/O	Ratio air/O
Nitrogen . .	77	3·35	4·35	79	3·76	4·76
Oxygen . .	23	1	1	21	1	1

Full information as to the weight and volume of both oxygen and air for combustion, the products of combustion, etc., for elementary fuel constituents, and the principal constituent gases of ordinary gaseous fuels, will be found in Table I, Appendix. An example of the method of calculation of these values is given below, the instance chosen being the combustion of carbon to carbon dioxide.

$$\begin{array}{rl}
 & \overset{\text{Carbon.}}{\mathrm{C}} + \overbrace{\mathrm{O}_2 + (\text{nitrogen})}^{\text{Air.}} = \overbrace{\mathrm{CO}_2 + (\text{nitrogen})}^{\text{Flue gases.}}\\
\left.\begin{array}{r}\text{Weight in}\\ \text{gm. or lb.}\end{array}\right\} & \begin{array}{l} 12 + 32 + (107) = 44 + (107)\\ 1 + \underbrace{2{\cdot}66 + (8{\cdot}93)}_{11{\cdot}6} = \underbrace{3{\cdot}66 + (8{\cdot}93)}_{12{\cdot}6}\end{array}
\end{array}$$

Volume in litres.

$$\left.\begin{array}{r}\text{At } 0^\circ\,\text{C.}\\ \text{and 760 mm.}\end{array}\right\}\begin{array}{l} 12 \text{ grams} + 22{\cdot}4 + (84{\cdot}2) = 22{\cdot}4 + (84{\cdot}2)\\ 1 \text{ gram} + \underbrace{1{\cdot}86 + (\ 7{\cdot}0)}_{8{\cdot}86 \text{ litres}} = \underbrace{1{\cdot}86 + (\ 7{\cdot}0)}_{8{\cdot}86 \text{ litres}}\end{array}$$

$$\left.\begin{array}{r}\text{At } 60^\circ\,\text{F.}\\ \text{and 30 in.}\end{array}\right\}\begin{array}{l} 12 \text{ grams} + 23{\cdot}60 + (88{\cdot}7) = 23{\cdot}60 + (88{\cdot}7)\\ 1 \text{ gram} + \underbrace{1{\cdot}96 + (7{\cdot}36)}_{9{\cdot}37 \text{ litres}} = \underbrace{1{\cdot}96 + (7{\cdot}36)}_{9{\cdot}37 \text{ litres}}\end{array}$$

Volume in cubic feet.

$$\left.\begin{array}{r}\text{At } 0^\circ\,\text{C.}\\ \text{and 760 mm.}\end{array}\right\}\begin{array}{l} 12 \text{ lb.} + 359{\cdot}0 + (1350) = 359{\cdot}0 + (1350)\\ 1 \text{ ,,} + \underbrace{30{\cdot}0 + (112{\cdot}5)}_{142{\cdot}5 \text{ cu. ft.}} = \underbrace{30{\cdot}0 + (112{\cdot}5)}_{142{\cdot}5 \text{ cu. ft.}}\end{array}$$

$$\left.\begin{array}{r}\text{At } 60^\circ\,\text{F.}\\ \text{and 30 in.}\end{array}\right\}\begin{array}{l} 12 \text{ lb.} + 378{\cdot}0 + (1421) = 378{\cdot}0 + (1421)\\ 1 \text{ ,,} + \underbrace{31{\cdot}5 + (118{\cdot}4)}_{149{\cdot}9 \text{ cu. ft.}} = \underbrace{31{\cdot}5 + (118{\cdot}4)}_{149{\cdot}9 \text{ cu. ft.}}\end{array}$$

Composition of flue gases (by volume).

$$\mathrm{CO}_2\% = \frac{29{\cdot}8 \times 100}{141{\cdot}8} = 21{\cdot}0 \qquad\qquad \mathrm{N}_2\% = \frac{112 \times 100}{141{\cdot}8} = 79{\cdot}0.$$

The volume (or weight) of oxygen or air for any fuel will be arrived at by the sum of the volumes (or weights) required by the ultimate constituents per lb. in the case of solid or liquid fuels, and in the case of gaseous fuels from the like quantities required for the separate combustible gaseous constituents per cubic foot of the whole gas.

In regard to gases Haslam has shown that it is approximately true that the theoretical amount of air required for combustion is a function of its gross calorific value. His equation for calculating the number of cubic feet of air required to burn 1 cubic foot of the gas is:

$$\text{cu. ft. air} = \frac{(\text{B.Th.U.})^{1{\cdot}08} - 52}{100}$$

Where less accuracy is required it can be taken that the heating value of rich fuel gases calculated in terms of heat units per cubic foot of theoretical gas-air mixture is approximately the same, i.e. 100 B.Th.U. The relationship is less true in regard to low-grade gases, e.g. it is about 87 B.Th.U. for water gas and 65 for producer gas.

Calorific Value. The calorific value is expressed in terms of various units of heat. For scientific purposes in this country the centigrade system forms the basis, but many practical men prefer the system based on the Fahrenheit thermometer scale, the results being expressed as British Thermal Units (B.Th.U.).

The *calorie* represents the quantity of heat necessary to raise 1 gram of water through 1° C. Three slightly different units are recognized, the 15°, the 20° and the mean calorie. In the first the gram of water is heated from 15–16° C., in the second from 20–21° C. and in the third from 0–100° C., divided by 100. The mean calorie and the 15° C. calorie are equivalent to $4 \cdot 184 \times 10^7$ ergs, while the 20° calorie is $4 \cdot 180 \times 10^7$ ergs. The 15° C. is used mainly in this country.

The Calorie (large calorie) is equal to 1000 gram calories.

The *British Thermal Unit* is defined as the amount of heat required to raise 1 lb. of water 1° F. (from 60° to 61° F.).

Suppose then a given unit of heat raises 1000 grams of water 1° C.; since 1000 grams = 2·2 lb., and 1° C. = 1·8° F., this same unit of heat would raise 1 lb. of water $2 \cdot 2 \times 1 \cdot 8 = 3 \cdot 96$° F., or, stated otherwise, 1 Calorie (kilogram degree centigrade unit) = 3·96 B.Th.U.; conversely, 1 B.Th.U. = 0·252 kilogram degree centigrade unit.

A fourth unit of heat—the *pound degree centigrade unit*, being the amount of heat required to raise 1 lb. of water 1° C., is frequently employed in stating the calorific value of solid and liquid fuels. It is related obviously to the B.Th.U. as are the centigrade and Fahrenheit thermometer degrees, namely

$$\frac{\text{Fahrenheit degree}}{\text{Centigrade degree}} = \frac{180}{100} = 1 \cdot 8$$

A concrete practical example will make this evident: 1 gram of coal burnt in a calorimeter raised the temperature of 3000 grams of water 2·5° C. Its calorific value $= 3000 \times 2 \cdot 5 = 7500$ calories. 1 lb. of coal would have obviously raised 3000 lb. of water $2 \cdot 5 \times 1 \cdot 8 = 4 \cdot 5$° F., or its calorific value $= 3000 \times 4 \cdot 5 = 13{,}500$ B.Th.U. The calorific values of all solid and liquid fuels referred to subsequently have this ratio between B.Th.U, and calories.

It is frequently convenient to express these values in foot-pounds

1 kilogram degree centigrade = 3087 foot-pounds
1 pound degree centigrade = 1400 „
1 British Thermal Unit = 778 „

Gross and Net Calorific Values. When a fuel containing hydrogen is burnt water is produced invariably, and if this water is condensed it gives up its latent heat as steam together with the heat liberated on cooling from its condensation point to the temperature of the calorimeter. The total calorific value, *gross*, or higher heating value of a fuel is the number of heat units liberated when unit weight of fuel (or volume, in the case of gases) is burnt and the products of combustion are all cooled to 60° F., the water vapour in them being condensed.

In many cases, however, this heat carried by the water produced from hydrogen during combustion, or stored in water evaporated from the fuel, is not available for conversion into work. Thus, it plays no part in raising the flame temperature of burning gases, or in developing energy in a gas engine. For all such computations it must be eliminated, and the value after this deduction is termed the *net* calorific value. This may be similarly defined to the gross value except that whilst the products are assumed to be cooled to 60° F. it is further assumed that *the water vapour does not condense.*

For gases in this country the unit is the cubic foot measured at 60° F. and saturated with water vapour.

No definite agreement is to be found in the literature on fuel as to whether the net value shall be deduced simply from the latent heat of steam, or whether by deduction from the gross of both the latent heat and sensible heat in cooling from 100° C. (212° F.); in the latter case it would be necessary to fix the temperature to which the products are finally reduced. In English practice it is usual to adopt the formula of the Heat Engine Trials Committee of the Institution of Civil Engineers, the *net* calorific value being calculated from the gross by deducting the latent heat (1055 B.Th.U. per lb.) of the weight of water condensed by cooling the products to 60° F.

The British Standards Institution has published authoritative definitions of gross and net calorific values (No. 526—1933) and recommends that they shall be respectively designated by the symbols H_s and H_i.

For many thermo-dynamic calculations the net value is of service, but its real value must not be misconstrued. The error has arisen that the net value is the true measure of the practical heating value of the fuel. Flue gases and exhaust gases are seldom cooled to anything approaching 100° C. (212° F.), and must carry away not only the latent heat units in the uncondensed steam, but all the additional sensible heat units in the flue gas, which will depend primarily on their temperature. To quote Professor C. V. Boys, under practical conditions "every user of gas should be equally entitled to a special net value to meet his requirements." The net value is a useful convention but is in reality an artificial figure.

Although the net calorific value at one time received official recognition as a standard in the case of coal gas, it is agreed generally that the gross value is the proper one to take, and the Gas Regulations Act (1920), which altered the whole system of charging consumers from one of cubic feet to "therms," specify the gross value. The inability of most of our appliances to convert all the heat units into other forms of energy is no logical basis for rating fuels on a value which is not their true one; indeed in some cases it is practicable to utilize at least a considerable proportion of the latent heat units. In the United States, where the calorific value of gas is considered rightly as of the highest importance, opinion is almost unanimous in favour of the gross value as the standard. In 1906, the Association of German and Austrian Engineers agreed that calorific values should be calculated on the assumption that the whole of the products are cooled to 100° C., with the water remaining as steam.

When it becomes a question of comparison between different samples of coal (unless of very different water content) or of oil, the net value offers so little advantage over the gross as to be negligible, because with coals of the same class, or oils of the same character, the hydrogen content is so similar in different samples, that the difference between the gross and net values is nearly constant. The extra labour involved in determining the hydrogen by the combustion process—the only method available giving the requisite accuracy—is not commensurate with the gain.

Calculation of Calorific Value. In general, actual determinations in some form of calorimeter are preferable to calculated values; comparison between the methods is dealt with under Calorimetry (p. 363), but the general method of calculating the values is referred to here in order that other points may be elucidated.

It is assumed in practically all such calculations that the heating value of the constituent elements of the fuel is the same as the value for these same elements in the free condition, and that no heat is generated beyond this, or no heat utilized in setting free the constituent elements in a condition for their combustion by oxygen, assumptions which certainly cannot be substantiated.

When carbon is burnt in oxygen with the formation of carbon dioxide, the weights of material involved and the heat evolved may be expressed by a *thermo-chemical equation*, thus:

$$\begin{array}{ccccccc} C & + & O_2 & = & CO_2 & + & 97{,}644 \\ \text{12 grams} & & \text{32 grams} & & \text{44 grams} & & \text{calories} \\ \text{Carbon} & & \text{Oxygen} & & \text{Carbon dioxide} & & \end{array}$$

and when hydrogen burns with the formation of water at constant pressure as:

$$\begin{array}{ccccccc} H_2 & + & O & = & H_2O & + & 69{,}000 \\ \text{2 grams} & & \text{16 grams} & & \text{18 grams} & & \text{calories} \\ \text{Hydrogen} & & \text{Oxygen} & & \text{Water (condensed)} & & \\ & & & & \text{Water (as steam)} & + & 58{,}100 \end{array}$$

It follows that 1 gram of carbon gives 8137 cals. (14,646 B.Th.U.), and 1 gram of hydrogen 34,500 cals. (62,100 B.Th.U.), if the steam produced is condensed to water at 0° C.; if the steam remains as such at 100° C., 29,050 cals. (52,290 B.Th.U.).

The calculated calorific value (gross) of any fuel containing only these two elements will be found from the equation:

$$\frac{(\text{Carbon }\% \times 8137) + (\text{Hydrogen }\% \times 34{,}500)}{100} = \text{calories (gross)}$$

A large number of fuels already contain oxygen, and therefore a smaller quantity of this gas will be required for their consumption, and the heat produced will be proportionately less. The assumption is made that any oxygen present is already wholly in combination with hydrogen ; again, this is certainly not the case, but since nothing is definitely known as to the actual distribution of oxygen between the hydrogen and other elements present, it affords the only possible working hypothesis. Since it is known that in water 8 parts by weight of oxygen are combined with 1 part of hydrogen, it is customary to deduct from the total hydrogen an amount equal to one-eighth of the oxygen present, calling the remainder the *available hydrogen*. The formula thus becomes :

$$\text{Calories (gross) per gram} = \frac{(\text{C}\ \% \times 8137) + \left\{\left(\text{H} - \frac{\text{O}}{8}\right) \times 34{,}500\right\}}{100}$$

In the most complete form, such as may be applied to coals, the following extended formula is employed :

$$\text{Calories} = \frac{\text{C} \times 8137) + \left\{\left(\text{H} - \frac{(\text{O} + \text{N} - 1)}{8}\right) \times 34{,}500\right\} + (\text{S} \times 2220) - (\text{H}_2\text{O} \times 600)}{100}$$

Here a fixed deduction of 1 per cent. is made for the nitrogen present in the fuel, this being regarded as a fair average, although somewhat low for English coals ; sulphur, in the form of pyrites, is regarded as furnishing heat, and an approximate deduction is made for the evaporation of the moisture present in the fuel.

In the case of gaseous fuels the calorific value must not be calculated from the elementary constituents, but from the sum of the calorific values of the constituent gases themselves, the values for which are well established, and are given in Table I, Appendix.

Exothermic and Endothermic Compounds. If the simplest of the formulæ on p. 14, that for a fuel containing carbon and hydrogen alone, be applied to the two gases, methane or marsh gas (CH_4) and acetylene (C_2H_2), it is found that in the case of methane the calculated value is much higher than that found by a calorimeter, whilst in the latter case it is considerably lower. Some of the heat is expended in breaking down the methane before combustion ; in the case of acetylene surplus heat is actually produced.

The explanation is to be found in the conditions attending the formation of the two gases. When methane is formed from its elements, carbon and hydrogen, heat is evolved, and to separate these elements again and enable them to enter into fresh combination with oxygen during the combustion, as much heat must be supplied as was given out originally. Compounds which evolve heat on formation are termed *exothermic.* Acetylene, conversely, absorbs heat on formation; this heat is evolved on decomposition, and adds to the heat generated by the combustion of its constituent elements. Compounds whose formation demands heat are termed *endothermic.*

It follows that all formulæ for calculating calorific values must fail unless the heat of formation of the fuel is either only slightly positive or negative. Such formulæ apply fairly well to most coals, simply because coal is very slightly endothermic, its endothermic character increasing with the amount of oxygen present. In the case of gaseous fuels, where the heat of formation of the constituent gases may be either markedly positive or negative, calculation from elementary composition will obviously give misleading results.

With gaseous fuels the results calculated from the values for the constituent gases at constant volume are found to be in good agreement with determinations made in calorimeters of the usual pattern—Junkers, Boys, etc.

It is important to note that the calorific value is higher when the fuel is burnt at constant pressure than it is at constant volume, for example, in cases where the final products occupy a less volume than the original, e.g. with hydrogen, where the steam occupies two-thirds of the former volume, and may ultimately condense to a negligible volume. In the case of actual determinations of calorific values of solid and liquid fuels in a bomb calorimeter, the difference is negligible, a few calories per gram in the case of coal.

Calorific Intensity. Whilst any given fuel is capable of developing on combustion a given number of heat units, the actual temperature attained by the combustion will depend not only on the calorific value but on a number of other conditions—the weight of the products of combustion and of any excess air, their specific heat and the heat losses which take place. Assuming that the whole of the heat is utilized without loss in raising the temperature of the products, then it is possible to calculate the maximum theoretical temperature attainable. Accurate knowledge of the actual variation in specific heat of gases with rise of temperature was for long wanting. Only in recent years has sufficiently accurate data on the specific heat of gases at high temperature been available. In practice it is seldom possible to attain the theoretical maximum because of inevitable heat losses through radiation and as sensible heat in the products.

Certain practical considerations however arise. Imagine a fuel is burning under a boiler, and a steady temperature has been attained, that is, the heat production and losses have reached a certain equilibrium. Increase of the rate of combustion by increasing the draught will not raise the amount of heat given out per pound of fuel, but the production of heat increases proportionately much faster than the loss of heat, consequently a higher calorific intensity is attained. Again, the use of excessive air for combustion will greatly lower the temperature owing to losses of sensible heat. The effect may be well illustrated with approximate figures for the combustion of hydrogen. With the theoretical volume of pure oxygen the theoretical attainable temperature is over 6000° C. (say 11,000° F.); with the theoretical volume of air 2300° C.; with twice the theoretical air 1400° C.

In the case of regenerative furnaces, where the waste heat from the gaseous products is utilized for heating up the air required for combustion (with the poorer gaseous fuels the fuel is heated also) it will be seen how greatly this must add to the calorific intensity of the reaction; indeed, the success of such low calorific value fuels as "producer gases" is dependent entirely on this possibility of increasing the intensity by regeneration. For example, the theoretical temperature for the combustion of carbon monoxide with twice its volume of air, both gases supplied at ordinary temperatures, is less than 1600° C., but if by regeneration the initial temperature of the combustible gas and the air is 500° C., then a temperature of a little over 2000° C. is theoretically attainable.

Evaporative Values. It is common practice to state the thermal value of a fuel in terms of its power of evaporating water from a temperature of 100° C. (212° F.) into steam at the same temperature. The evaporative value will therefore equal $\frac{\text{Calories (or B.Th.U.)}}{\text{Latent heat of steam}}$. In calories per gram the denominator will be 536·5; in B.Th.U. per lb. 966.

The latent heat of steam (or latent heat of vaporization) falls with increase of temperature (i.e. higher boiler pressures). According to Regnault, up to 230° C. (404 lb. absolute pressure), it equals $606{\cdot}5 - 0{\cdot}695t$, where t equals the boiling temperature. The important point, however, in practice is the total amount of heat in steam at a given temperature. This obviously will be the sum of the latent heat of vaporization and heat required to raise the water from feed temperature to its boiling-point. According to Regnault, the feed being 0° C. (32° F.), the value for the total heat up to 230° C. is equal to $606{\cdot}5 + 0{\cdot}305t$ calories. From this value the temperature of the feed water must be deducted. The value in B.Th.U. will be 1·8 times as great.

As an example, a boiler is worked at 115 lb. absolute pressure; the feed water is at 15·5° C. (60° F.). At this pressure the water boils at 170° C. (338° F.). The total heat equals $606{\cdot}5 + (0{\cdot}305 \times 170) =$ 658 cals. or 1184 B.Th.U. The heat required to convert 1 kilogram of water to steam under these conditions will be $658 - 15{\cdot}5 = 632{\cdot}5$

cals., or 1 lb. of water 1138 B.Th.U. If the coal has a calorific value of 7500 calories (13,500 B.Th.U.), the theoretical evaporative power will be $\frac{7500}{632\cdot5}$ or $\frac{13{,}500}{1138} = 11\cdot8$ lb.

Limits of Combustion. Mixtures of combustible gases or vapours with air are capable of burning only within fairly well-defined limits. Quoting from Burgess and Wheeler (*Trans. Chem. Soc.*, 1911, 2013)—"To ensure propagation of flame, it is necessary (1) that the initial source of heat should be of a volume, intensity and duration sufficient to raise the layer of gases in its immediate vicinity to a temperature higher than, or as high as, the ignition temperature of the mixture; and (2) that the heat contained in the products of combustion of this first layer should be sufficient to raise the adjacent layer to its ignition temperature."

"The Smallest Quantity of any Combustible Gas which, when mixed with a Given Quantity of Air or Oxygen, will enable this Self Propagation of Flame to take place, is termed the Lower Limit of Inflammation of the Gas."

A "lower limit mixture" is one such that a given volume must, under the conditions of its combustion, evolve just sufficient heat to raise an equal volume to its ignition temperature. There are three factors which determine this—(1) the calorific power of the gas, (2) the relative volume and specific heat of the diluent gases, (3) the ignition temperature of the mixture.

The explosive range of mixtures is of considerable importance from the point of view of risks of accident from the escape of gases (or vapours) into the air, besides having an important bearing on the practical use of such mixtures in engines.

The upper and lower limits are greatly influenced by a number of factors, e.g. the shape and size of the vessel; whether the flame is propagated downwards, upwards or horizontally, and by pressure and temperature.

The effect of the size of the tube and the direction of propagation is well shown in A. G. White's results (*J.C.S.*, 1924, **124**, 2387) with all gases, those for acetylene being:

	Tube 7·5 cm.			5 cm.			2·5 cm.		
	U.	H.	D.	U.	H.	D.	U.	H.	D.
Low . .	2·6	2·68	2·78	2·6	2·68	2·8	2·73	2·87	2·9
High .	>80·5	78·5	71·0	78·0	68·5	63·5	70·0	59·5	55·0

The effect of temperature and pressure in the upper and lower limits is of considerable importance, since in the cylinder of an engine the charge is always under compression at the moment of ignition, and is heated by the compression and contact with the hot walls of the cylinder. Increase of temperature extends the explosive range, thus Mason and Wheeler (*J.C.S.*, 1918, **113**, 45) give the following figures for methane/air mixtures with downward propagation of flame :

Temp. ° C.	Lower limit. Per cent.	Higher limit. Per cent.	Range. Per cent.
20	6·00	13·40	7·40
100	5·45	13·50	8·05
200	5·05	13·85	8·80
300	4·40	14·25	9·85
400	4·00	14·70	10·70

The effect of pressure with hydrocarbon/air mixtures is to steadily raise the upper limit, whilst with the lower limit mixtures moderate pressure lowers the lower limit, but as the pressure is increased further the lower limit again rises. The result, however, always is to widen the explosive range. Data for the earlier paraffin hydrocarbons have been published by Payman and Wheeler (*J.C.S.*, 1923, **123**, 426).

White (*loc. cit.*) gives a valuable summary of previous results and new data from his own investigations. These are summarized in Table III, the results being for 7·5-cm. tubes and upward propagation, which, without exception, gives the extremes.

TABLE III

Explosive Limits of Gases with Air (*White*)
In 7·5-cm. tubes—upward propagation

	Lower.	Upper.		Lower.	Upper
Hydrogen	4·15	75·00	Ethylene	3·02	34·00
Carbon monoxide	12·80	72·00	Propylene	2·18	9·70
Methane	5·35	14·85	Butylene	1·70	9·00
Ethane	3·12	14·95	Acetylene	2·60	>80·50
Pentane (*n*)	1·42	8·00			

Additional results for important commercial gases and vapours are given in Table IV (p. 20).

The explosive range of gasoline (petrol) was given in the Motor Union Fuel Report (1907) as 1·5 to 5·3 per cent., and by Burrell and Gauger (*loc. cit.*) as 1·5 to 6 per cent.

For pentane vapour, in a large globe with central ignition, Burgess and Wheeler found the limits to be 1·4 and 4·5 per cent. Payman and Wheeler, for downward propagation, found 1·75 and 4·68 per cent.

Velocity of Flame Propagation. The speed at which a flame will travel through a gas/air mixture is of importance in the design

TABLE IV

EXPLOSIVE LIMITS OF GASES AND VAPOURS WITH AIR

Gases

	Lower limit.	Upper limit.	Authority.
Coal gas	7·90	19·0	Bunte.[1]
	7·0	21·0	Burrell and Gauger.[2]
Water gas	12·40	66·75	Bunte and Eitner.
Natural gas	5·0	12·0	Burrell and Gauger.
Blast furnace gas . .	36·0	65·0	„ „

Vapours

	Upwards.		Downwards.		Authority.
	Lower.	Upper.	Lower.	Upper.	
Acetone	2·89	12·95	2·93	8·60	White.[3]
	—	—	2·35	8·50	Payman.[4]
Alcohol, ethyl . . .	3·56	18·0	3·75	11·50	White.
	—	—	4·0	13·60	Payman.
Alcohol, methyl . . .	7·05	36·50	7·45	26·50	White.
	—	—	7·80	18·0	Payman.
Ether, ethyl	1·71	48·0	1·85	6·40	White.
	—	—	1·80	5·20	Payman.
Benzene	1·41	7·45	1·46	5·55	White.
	—	—	1·40	4·70	Payman.
Toluene	1·27	6·75	1·28	4·60	White.
	—	—	1·40	4·70	Payman.
Carbon disulphide . .	1·06	50·0	1·91	35·0	White.
	—	—	4·10	—	Payman.

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[1] Bunte (*Journ. Gasbeleucht.*, 1901, **44**, 835).

[2] Burrell and Gauger (*U.S. Tech. Paper*, No. 150, 1917).

[3] White (*J.C.S.*, 1922, **121**, 1244), in tubes up to 7·5 cm.

[4] Payman (*J.S.C.I.*, 1918, **37**, 406 R).

of gas burners and combustion spaces. Too high a speed may mean overheating of the burner or too localized heating of the furnace. In ordinary flame combustion the rate is not only influenced by the proportions of gas and air but also by the shape of the chamber in which combustion takes place. The usual laboratory method of determining velocities is to pass the combustible mixture through a tube at such a velocity that the flame, started at the outlet end, just fails to strike back or to ignite stationary mixtures. These conditions are similar to those obtaining in gas burners and furnaces but are widely removed from those in an explosion engine where there is always turbulence, and combustion, except with very weak mixtures, is very rapid. Wheeler has shown that with excessive turbulence (a rapidly rotating fan in the mixture) flame is not so readily propagated, but if it does spread (moderate turbulence) it travels much more rapidly than when the mixture is at rest. The effect of turbulence, however, is not nearly as great with rapidly burning mixtures as with weak slow-burning ones.

The highest velocity of flame propagation does not occur when the proportions of gas (or vapour) with air are theoretically correct for perfect combustion, but is found at a point near the middle, between the upper and lower combustible limits. At either end of the scale Payman (*J.C.S.*, 1919, **115**, 1444) has shown, in the case of the first five members of the paraffin series, that the rate is approximately 20 cm. per second

When flame propagation is studied by the tube method it is found that the rate decreases with the diameter of the tube to a marked extent, the speed in a 1-inch tube being less than half that in a 12-inch tube. If comparisons of the different fuel gases are made under more than one set of conditions the curves are found to be of the same general shape but of very different dimensions. At low gas percentages the rate of propagation is low; as the percentage increases the rate increases to a maximum and then decreases again as the upper limit of inflammability is approached. Table V summarizes the values for the maximum rates for a number of gases, while Figure 1 illustrates the shape of the curves.

TABLE V

MAXIMUM SPEED OF UNIFORM MOVEMENT OF FLAME IN MIXTURES WITH AIR IN HORIZONTAL TUBES

Gas.	Per cent. in mixture.	Speed cm. per sec.	Diam. of tube cm.	Authority.
Hydrogen . .	(about) 38	(about) 490	2·5	Haward and Obagawa (*J.C.S.*, 1916, **109**, 83).
Methane . . .	9·5	66	2·5	Payman (*J.C.S.*, 1919, **115**, 1446).
,, . . .	9·6	91	5·0	Mason (*J.C.S.*, 1923, **123**, 212).
Ethane . . .	6·5	86	2·5	Payman.
,, . . .	6·0	127	5·0	Mason.
Propane . . .	4·7	82	2·5	Payman.
,, . . .	4·5	114	5·0	Mason.
Butane . . .	3·7	83	2·5	Payman.
,, . . .	3·6	113	5·0	Mason.
Pentane . . .	3·0	82	2·5	Payman.
,, . . .	2·9	115	5·0	Mason.
Ethylene . . .	7·2	142	2·5	Chapman (*J.C.S.*, 1921, **119**, 1678).
Acetylene . .	8·9	282	2·5	Mason and Wheeler (*J.C.S.*, 1917, **111**, 1044).
,, . .	8·9	312	5·0	,, ,,

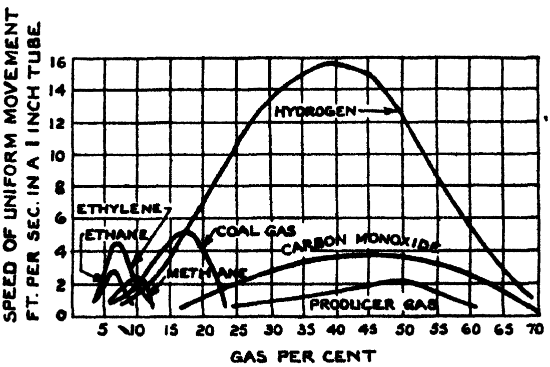
The outstanding behaviour of hydrogen is readily seen in this figure.

It has been shown that, under the above conditions, the lowest speeds, i.e. those of the limiting mixtures, are the same for all gases at about 0·65 ft. per sec. It is also an important fact that the velocities are affected by the presence of moisture, that of carbon monoxide, for example, being considerably increased.

It is possible to calculate from the composition of a coal gas what are the proportions for the mixtures representing the upper and lower limits of inflammability and that giving maximum flame velocity.

$$L_x = \frac{a + b + c +}{\frac{a}{L_a} + \frac{b}{L_b} + \frac{c}{L_c} +}$$

Where L_x is the required limit or maximum, a, b, c, the percentages of the gas constituents and L_a L_b, etc., their corresponding limits or maxima. This formula cannot be applied in the case of gases high in nitrogen, e.g. producer gas.



FIG, 1.—Speed of Uniform Movement of Flame of Gases in Air.

Flame Temperature. Flame temperature is of importance in gas heating partly because the higher the flame temperature the more rapid the rate of heating and partly because the higher the flame temperature the greater the thermal efficiency of the process.

Actual flame-temperatures are difficult to measure and the values normally used are those of the "theoretical" temperature, i.e. that which would be developed if the heat of combustion heated only the products of combustion. Theoretical flame temperatures can therefore be calculated from the heats of combustion, specific heats, and volumes of the gases. These values are, of course, higher than the practical values, but are of importance in being strictly comparable and serve for the calculation of effects of pre-heating, excess air, etc. Values for certain of the common gases are:

	B.Th.U. per cu. ft.	Flame temp. ° F.
Coal gas	560	3910
Water gas	310	4170
„ „ carburetted . . .	529	4090
Producer gas	128	3050
Blast furnace gas	92	2660

In calculating these values the lower (net) heat of combustion of the gases is used since latent heat is not effective at temperatures above 212° F.

The flame temperatures of mixed gases can be calculated from tables or graphs showing the total heat content of the products of combustion which are mainly CO_2, N_2 and H_2O. The "theoretical" temperatures are for cold gas and the theoretical amount of cold air. They are decreased by the addition of excess air and increased by pre-heating either air or gas. In practice the calculated flame temperature is not realized: (1) because the data, especially specific heats, used for calculating is not too exact, (2) some dissociation of the products CO_2 and H_2O occurs, (3) the flame radiates heat to the extent of 5–20 per cent. and (4) since combustion takes an appreciable time heat is lost by convection and conduction.

The losses under (3) and (4) depend upon specific conditions, but those under (2) can be calculated from known data and should be applied wherever possible by deducting the heat of dissociation from the heat of combustion of the gas. Since heat is absorbed by the dissociation the corrected temperatures are appreciably lower than the uncorrected; CO, for example, being reduced from 4500 to 3750° F.

In practice high flame temperature is achieved (1) by rapid combustion, (2) by reducing excess air to a minimum, and (3) by pre-heating. An increase of excess air from 0 to 100 per cent. will reduce the flame temperature of producer gas from about 3050° F. by some 30 per cent. The same gas pre-heated to 1000° F. and burned with pre-heated air at 1000° F. showed an increase of flame temperature of about 20 per cent. to 3800° F. Since dilution and pre-heating are such important factors in practice arrangements are made in most modern furnaces for heat interchange from flue gas to combustion gas or air and, where dilution is necessary, to achieve this by the circulation of hot flue gas rather than by increasing the excess air.

Heat interchange is achieved either by regeneration or recuperation. The former process is discontinuous, the hot gases giving up their heat in a checker brickwork chamber for a short period and the chamber giving up its heat again to the gas or air. Two chambers operated alternately at short time intervals form a complete system. Recuperation is a continuous process, heat being given to the gas or air from the hot flue gases through brick or metal partitions, the gases flowing counter-current to one another.

Space does not permit of a discussion of the design or respective merits of regenerators or recuperators. It is sufficient to say that the former are generally used where a high degree of pre-heat is required. They do not suffer from possible leakage of flue gas into the air stream but do suffer from greater operating cost and from the variability of the air temperature.

CHAPTER II

WOOD, PEAT, AND MINOR SOLID FUELS

Classification of Fuels. Fuels are employed in the solid, liquid and gaseous condition. The solid fuels are essentially naturally occurring materials, principally wood, peat, and coal, although for special purposes they are carbonized for the production of charcoal and coke. Liquid fuels are mostly direct natural products, such as the petroleum oils, but considerable quantities are obtained as the result of destructive distillation of solid fuels (tars, etc.); whilst gaseous fuels occur naturally only to a very limited extent (natural gas), but are mainly the result of destructive distillation of solid fuels (coal gas, coke oven gas) or liquid fuels (oil gas), or the result of the incomplete combustion of solid fuels in gas producers either by an air blast (producer gas), steam (water gas), or a combination of air and steam (Dowson or semi-water gas).

With such a large variety of materials available classification is difficult, but the following is a general scheme.

General Scheme of Classification of Fuels

Natural fuels	Unchanged	Wood; spent tan; cokernut shells, etc. Fatty oils—fish, palm, etc. Natural gas.
	Metamorphosed	Peat (slightly). Coal (in varying degree). Mineral oils (completely).
Prepared fuels	By destructive action of heat on natural fuels	Charcoal, coke.. Tars, benzole (shale oil). Coal and coke oven gas.
	By "limited" combustion	Producer gas; water gas.
	By fermentation.	Ethyl alcohol.
	By synthesis	Methyl and ethyl alcohol.
	By hydrogenation	"Motor spirit"; tetralin.

The chief solid fuels are as follows:

Wood	=	Wood charcoal
Peat	=	Peat charcoal Briquettes
Lignites and coal . . .	=	Coke Briquetted fuels

In addition to the above important solid fuels, large amounts of various waste materials are frequently available in certain industries —spent tan, bagasse (the residue of canes after sugar extraction), Nile sud, coconut and other nut shells, etc.

WOOD

Composition and Thermal Value of Wood. The abundance of wood throughout man's existence, its comparatively rapid growth and reproduction, and the ease of obtaining supplies, naturally made it one of the earliest and most generally used of all fuels. At the present time it is only of importance as a fuel in countries where large forests still remain.

The combustible portion of all woods consists of a modified form of cellulose lignin, which contains a higher percentage of carbon and oxygen than the cellulose from which it was derived. Cellulose approximates to the empirical formula $n(C_6H_{10}O_5)$, the percentage composition being $C = 44{\cdot}44$; $H = 6{\cdot}17$; $O = 43{\cdot}39$ per cent. In many woods, more particularly the coniferous, considerable quantities of resinous substances of much higher calorific value than lignin are found. It will be noted that in cellulose the hydrogen and oxygen are present in the proportions existing in water—in other words, as far as calorific effect is concerned the hydrogen is negligible, and the heating value is dependent on the carbon and any resinous constituents present. The average calorific value of cellulose is 4150 calories (7500 B.Th.U.).

The average composition and thermal value of dry wood is given in Table VI.

TABLE VI

Composition and Calorific Value of Dry Wood

	Pounds per cu. ft.	Carbon.	Hydrogen.	Oxygen.	Ash.	Calories per kilo.	B.Th.U. per lb.
Ash . .	46	49·18	6·27	43·91	0·57	4710	8480
Beech . .	43	49·06	6·11	44·17	0·57	4774	8591
Elm . .	35	48·89	6·20	44·25	0·50	4728	8510
Oak . .	52	50·16	6·02	43·36	0·37	4620	8316
Fir . . .	—	50·36	5·92	43·39	0·28	5035	9063
Pine . .	30	50·31	6·20	43·08	0·37	5085	9153

In general, woods containing much resinous matter, as with fir, pine, etc., exhibit a higher calorific value, a pine knot examined by Slossen giving about 6005 calories (10,860 B.Th.U.).

Perfectly *dry* wood, therefore, is but a poor fuel from the point of view of thermal value, but in practice the best attainable condition is that resulting from prolonged air-drying. When freshly cut the moisture in different woods varies throughout a wide range, from 26 per cent. in willow to over 50 per cent. in poplar. Great variation is also found in the same wood at different seasons and in different parts of the plant. By proper air-drying the range of moisture content is reduced, so that it lies usually between 15 and 20 per cent. Low as is the calorific value of perfectly dry wood, it is apparent that the value is still further reduced by the presence of this residual moisture.

Under the most favourable conditions wood will be of low value as a fuel, for (1) only some 80 per cent. is actual combustible; (2) the calorific value of this combustible is low; (3) the large amount of moisture present demands much of the available heat for its vaporization. On the other hand, wood is easy to ignite, and is for that reason employed largely to kindle less easily ignited fuels; it can be burned completely without difficulty, and contains but little ash, seldom exceeding 1 per cent. on the air-dried material. The composition of the ash is very variable, but since the amount is so small it is a factor of such minor importance from the fuel point of view that its further consideration is unnecessary.

Wood has been used for the production of town's gas from quite early times. The yield from dry firwood, carbonized at 1200° C., is about 30,000 cu. ft. per ton, with a calorific value of some 360 B.Th.U. per cu. ft.

Wood gas consists of CO_2, 13; hydrocarbons, 2; carbon monoxide, 24; hydrogen, 45; methane, 15; nitrogen, 1 per cent. The charcoal yield is about 19 per cent. of the dry wood. Wood, and especially waste wood, has also been used successfully for the manufacture of producer gas. Wood for this purpose may contain as much as 50 per cent. of moisture. A typical wood-producer gas contains CO_2, 9; CO, 25; H_2, 10; CH_4, 3; N_2, 53 per cent.; calorific value 143 B.Th.U. per cu. ft.

Wood Charcoal. Wood charcoal is obtained by the destructive distillation of wood which, if carried to completion, leaves a residue retaining the original shape and structure of the wood, and which consists almost entirely of carbon. With lower temperatures the distillation is less complete, and combined hydrogen and oxygen are left to a greater or less extent in the mass.

By carbonization there is necessarily a large loss of heat units in the liquid and gaseous products, and the yield of solid fuel is very low. Although wood contains from 49 to 50 per cent. of carbon, under the most economical conditions of carbonizing in retorts 27 per cent. is the highest attainable yield. Wasteful as the process usually is unless careful attention is paid to utilization of the liquid tars, etc., certain great advantages result. Since the useless constituents of the wood, the combined hydrogen and oxygen, are mostly removed, the charcoal has a high calorific value, 11,000 to 13,500 B.Th.U., and owing to its porosity and combustion without flame it has high calorific intensity. Since concentration results the ash will be considerably higher than in the original wood.

Charcoal was formerly a metallurgical fuel of great importance, and the production at one time was so large as to cause complete denudation of forests, so that restrictive legislation on the output was imposed.

The introduction of coke and raw coal for iron smelting has displaced charcoal entirely from its position of importance, and now its use as a fuel is confined almost wholly to certain metallurgical operations where great purity of fuel is desired, for owing to the low mineral content and freedom from sulphur, phosphorus, etc., charcoal has great advantages.

Production of Charcoal. This was at one time carried out entirely by restricted combustion in heaps, a portion of the wood furnishing the necessary heat for the carbonization of the remainder. This process is necessarily wasteful, the yield seldom exceeding 15 per cent., and at present it is confined to countries where waste is not considered or where deforestation is a desired object. If the wood had a calorific value (dry) of 8500 B.Th.U., the yield of charcoal was 20 per cent., and of the highest calorific value, 13,000 B.Th.U., the actual percentage of heat units in the product would be about 30.

The production of charcoal by dry distillation of wood in closed retorts, externally heated, enables valuable by-products to be recovered. Where charcoal production is the primary object the distillation is carried out at a high temperature, and the liquid distillate is Stockholm tar or wood creosote, which, owing to its great preservative value, is employed largely for creosoting timber.

Distillation of wood, however, is now largely practised, especially in the United States, more particularly for the valuable liquid products, and charcoal is the by-product. In order not to impair the value of these products the temperature employed is lower than for complete carbonization. In practice oil-heated retorts are used with an initial temperature of 200° C. (392° F.) and finishing temperature 330–340° C. (625° F.). The yield of the various products per cord of wood (4000 lb.) is:

Best turpentine	40 gallons
Light oils	16 „
Heavy oils	128 „
Charcoal	950 lb.

In addition to the liquid products of distillation large volumes of gases are also evolved during the process. Lawrence (*J.S.C.I.*, 1911, 728) gives the following analysis of such gases:

	Per cent.
Heavy hydrocarbons	8·2
Methane	12·3
Carbon dioxide	31·4
Carbon monoxide	35·1
Hydrogen	10·9
Nitrogen	2·1

Charcoal obtained as a by-product is not of high quality; the wood is selected as far as possible to give the most valuable distillates and not for the production of charcoal primarily, and further the low temperatures employed do not permit of complete carbonization.

It is of interest to note that the destructive distillation of wood involves a strong exothermic reaction which, according to Fawsitt and Klason, sets in at 275° C. Hornsey estimates that 12 per cent. of the heat of combustion of the wood thus becomes available for the distillation process.

In many wood-producing countries very large quantities of otherwise waste wood are available for treatment for by-products and charcoal.

Lawrence (*J.S.C.I.*, 1918, **37**, 5 T.) gives the following yields of products from rich and lean woods:

TABLE VII

PRODUCTS FROM WOOD DISTILLATION

Products.	Rich wood (4 cords = 16,600 lb.).	Lean wood (4 cords = 16,000 lb.).
Charcoal	4284 lb.	4400 lb.
Refined turpentine	41·5 gals.	20·75 gals.
Pine oil	11·6 „	4·2 „
Resin spirit	21·5 „	12·0 „
Resin oil	141·0 „	64·75 „
Creosote oil	46·5 „	21·0 „
Wood alcohol	6·0 „	9·6 „
Calcium acetate (80 per cent.)	300 lb.	350 lb.
Pitch	1400 „	625 „

Composition and Properties of Charcoal. If distillation is carried out to the highest extent the products should be simply carbon and ash. Charcoal, however, has enormous absorptive powers for gas and is fairly hygroscopic. After exposure to air, even when fully carbonized, it contains much occluded gas and moisture, up to 8 or 9 per cent. If incompletely carbonized, it retains in combination hydrogen (2 to 3 per cent.) and oxygen (12 to 14 per cent.).

If charred at quite low temperatures red charcoal (rothköle, charbon roux) is obtained, and this contains actually a higher percentage of combustible than the high temperature product.

During recent years special attention has been directed, especially by the French Government, to the production of charcoal for use in small portable producers for driving automobiles with producer gas. The utilization of waste wood in the French forests was expected to replace an appreciable amount of the imported petrol. Governmental support gave an impetus in 1927 to the building of portable kilns and the design of producer-driven vehicles in France. Such vehicles are also of interest in our colonies where wood is available in quantity. Information regarding progress in this direction is available in the Reports of the Rallyées des Carburants Nationaux of the Automobile-Club de France. A comprehensive Colonial paper is that of Rennie (*Trans. Inst. Eng., Australia*, 1930, **2**, 101). Rennie shows that 16 lb. of charcoal is equivalent to 1 gallon of petrol, and quotes lorry tests which show 0·240 lb. charcoal per ton-mile against 0·144 lb. petrol. Under these conditions charcoal at 5·1*d.* per 16 lb. compares favourably with petrol at 22*d.* per gallon.[1]

PEAT

Importance of Peat. Enormous quantities of peat are available for fuel purposes, but owing to the situation of the bogs in sparsely populated districts, difficulties in removal of the excessive water, to its low density and low calorific value, its utilization has been only on a comparatively small scale. A D.S.I.R. report quotes the 1921 world production at only about 4 million tons. The production has definitely increased since then and in Russia alone 7·5 million tons were manufactured in 1928 (Paper R 5, World Power Conference, London, 1928).

In Europe the peat area is estimated at 140 million acres, whilst in Great Britain and Ireland there are approximately 2 million acres; in Ireland alone Frank estimates the available peat as equal to 2500 million tons of coal. Of the colonies, Canada is possessed of some 30 million acres. In the latter country, exhaustive inquiries were made in 1913 into the possibilities of economically using the vast peat accumulations, and valuable reports have been prepared by Haanel (*Can. Dept. of Mines*, No. 299, 1914) and Larson (*Can. Dept. of Mines*, Peat Bull. No. 4). The utilization of peat on any scale is mainly dependent on the cost of excavation and handling of the large quantities of such wet, raw material, and removing the large excess of water, a process which must always precede its use as fuel.

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[1] For further information on the utilization of wood and its products, the reader is referred to the *Destructive Distillation of Wood*, by H. M. Bunbury (Benn Bros., 1923), or *Wood Products*, by P. Dumesny and J. Noyer (Scott, Greenwood & Son, 1921).

Formation of Peat. Peat consists of partially decomposed vegetable matter, the result of luxuriant growth of lower forms of plant life, mostly mosses, under such favourable conditions as moisture and temperate climate. While the lower part of the stem dies off the upper part continues its growth, so that in the course of time a thick deposit results; as the under portions become buried deeper and deeper in the swamp decomposition through bacterial and other agencies progresses. The result is that whilst the upper parts of the bed are a matted, water-saturated sponge, the lower portions have largely lost their vegetable characteristics, and have become a semi-solid brown to black mass, in which greatly disintegrated vegetable structure is visible under the microscope.

When sufficiently felted together the upper parts of peat bogs can be cut into blocks and air-dried to give a bulky and porous fuel. A denser fuel is obtained by macerating the peat, pumped from the bog by any suitable means, and extruding the macerated material in layers for drying in the air. The raw peat consists of two distinct materials, plant residues and peat humus. The latter swells greatly in water but forms a hard mass on drying. Shrinkage is prevented in the hand-cut peat by the presence of plant remains, but when these are macerated in the case of machine-cut peat greater shrinkage becomes possible and the fuel becomes denser. In addition, the humus after drying will no longer absorb water to the same extent. The increase of density may be as much as from 0·4 to 0·8.

Moisture in Peat. The amount of solid matter in even a well-drained bog is small, amounting to from 10 to 16 per cent. The water content of peat at an exposed face or bank may be 88 per cent., but at the actual surface may be much lower. Hand-cut sods will usually contain from 88–90 per cent. of water. P. Purcell in the Report of the Director of Fuel Research (H.M. Stationery Office, London, 1922–23), quotes water/dry peat ratios as follows:

Very wet peat	19
Undrained bog	13–14
Cut peat	9
Lowest for raw peat	6–7
Air-dried peat	0·33

These ratios show clearly the amounts of water associated with say one ton of dry peat at different stages.

On complete air-drying, peat reaches an equilibrium with the air at from 13 to 18 per cent. of moisture. In practice the water content is seldom below 20 per cent. and the inner portions of the blocks of peat seldom reach so low a figure. It has been estimated that, for domestic requirements, the moisture content should not exceed 30–35 per cent. and, for industrial purposes, not more than 30 per cent.

Peat Drying. It is not possible to reduce the water content of raw peat by pressing or filtration. J. W. Hinchley (*J.S.C.I.*, 1922, **41**, 365 T.) has shown that a pressure of 800 lb. per sq. in. will not reduce the water content below 75 per cent. and that any filtering medium is rapidly choked by colloidal matter. By using steam in the press this figure can be reduced to about 60 per cent. Several processes of this type have been tried, but none have yet achieved success.

The most widely practised methods are those of air-drying on prepared surfaces near the bog. Since this air-drying depends upon climatic conditions the drying can be done only during the summer months. In Ireland where the climate is moist the peat-winning season lasts only 160–200 days. Cut peat dries more slowly than macerated peat. Purcell has shown that, during July and August in Ireland, the relative times of drying are respectively 30–40 days and 60 days. Similar drying periods have also been quoted for Russia.

The conditions of drying are important, the freshly formed peat is dried as deposited until it is firm enough for handling (water/peat ratio 5) and then " footed " or built up into heaps for further drying. Footed peat is stated by Purcell to have dried to a water ratio of 2 in 18 days as against 26 days for flat-spread peat.

In the preparation of machine peat the extruded material is cut into blocks on the field. (See Paper R 5., World Power Conference, 1928, describing work in the Russian fields.) The original thickness of the layers is not more than 20 cm. and the dried briquettes are approximately 5 cm.

The stages in drying are quoted as follows:

	Start.	Turning.	Stacks of Five.	Heaps.	Dumps.
Moisture per cent. . .	88	84	79	70–50	25
Time (days)	—	7–12	7–10	14	28–36 Total
Shrinkage V_0/V_t . . .	0	1·5	2·6	3·4–4·0	4·3

The finished bricks may be 25 × 5 × 5 cm.

Composition of Dry Peat. The composition of the pure peat substance, i.e. with water and ash eliminated, varies over only a moderate range. The following data are mainly from analyses by Bunte on Bohemian peats, and by Brame on British peats. There is quite close agreement between the results in each case:

	Limit.	Average.
Carbon	**56–63**	**57·5**
Hydrogen	**5·7–6·3**	**6·1**
Sulphur	**0·6–1·0**	—
Nitrogen	**1·3–2·7**	—
Oxygen	**31–38**	**34·9**

The ash in peat is a very variable quantity. It is exceptional to find less than 3 per cent., but not uncommon for over 10 per cent. to be present, most of which is undoubtedly due to infiltration. The lower layers will contain usually high ash as compared with the felted peat.

An analysis of a typical Irish Peat is given in Fuel Research Technical Paper 4 (1921) as carbon, 60·1 ; hydrogen, 5·8 ; sulphur, 0·6 ; nitrogen, 1·4 ; oxygen, 32·1 per cent.

The volatile matter in peat varies with its position in the bog. Purcell gives an example for different Irish peats :

	Volatile matter.	Ash.
Brown peat, Ticknevin	67·2	1·0
Black ,, ,, ...	65	7 8
Dense black peat	65·5	7·1
Light fibrous peat, Denbigh Moor .	70·4	0·7
Dense black peat, ,, ,, .	61·8	15·2

Calorific Value of Peat. On the air-dried peat this will be naturally a very variable factor for the same peat, owing to moisture variation under different conditions. For air-dried peat, 25 per cent. of moisture, Ekenberg takes an average of 3450 calories (6230 B.Th.U.).

Calorific value also varies with the position of the peat in the bog. Irish peat (Director of Fuel Research, 1922–3) provides the following data from Lullymore bog :

Depth (feet).	Ash per cent.	B.Th.U. per lb. dry.	Dry, ash free.
2	0·89	8917	9000
5	1·14	10,113	10,230
8	3·10	9260	9560
12	4·39	9548	9990

The average value for Turraun peat is quoted as 9262 B.Th.U. for an ash content of 4·54 per cent. or 9700 B.Th.U. for the pure peat. Rather higher figures are given in Fuel Research Technical Paper 4, of 9590 and 9640 B.Th.U. for peats containing 4·31 and 4·59 per cent. of ash. The pure peat has in this case a calorific value of 10,060 B.Th.U. per lb. Taking a good commercial peat at 20 per cent. of moisture and 3·5 per cent. of ash it should have a calorific value of 7700 B.Th.U. per lb. Its specific gravity should be just under 1·0.

Use of Peat as a Fuel. The methods may be classified as :

1. Direct burning of air-dried peat briquettes or dried peat powder.
2. Conversion into peat charcoal.
3. Briquetting after semi-carbonization (Ekenberg process).
4. Gasifying.

Peat, either hand-cut or machine-won, has a considerable application as a domestic fuel in countries where coal is not available. For commercial purposes its high cost of winning in a dry state has militated against it. In Ireland extensive experiments have been made but have now been discontinued. Better progress has been made in Northern Europe, mainly Sweden and Russia, and machine-won peat has been used fairly largely for power production. It is unlikely that hand-cut peat will ever become a commercial proposition in the same way.

As a boiler fuel dry peat (20–30 per cent. moisture) is a perfectly satisfactory fuel in the form of the blocks produced by air-drying, or in briquetted form. Paper R 6 (World Power Conference, 1928) describes satisfactory results obtained in Russian power stations in which as high thermal efficiency was obtained as with coal.

The problem of high moisture content has given rise to much experiment with artificial drying and perhaps the most important process is that of drying in the form of powder followed by briquetting. In the " Hydro peat " process the peat is pumped from the bog, coagulated with ferric hydrate, vacuum-filtered, and pressed (50 atmos. pressure) with the addition of 10 per cent. dry peat powder. At this stage the peat contains 60 per cent. moisture. The drying is then completed in rotary driers, using exhaust steam at 50 lb. pressure, to 15–18 per cent. moisture. The dry peat is then briquetted without a binder at 1200 atmospheres pressure in stamp presses. An average briquette is 5 × 6 × 18 cm. and has a density of 1·27. These have a high packing capacity of 77 lb. per cu. ft. or only 30 cu. ft. per ton.

Peat Powder. Peat powder has found somewhat extensive use on the Swedish State railways, being excavated and prepared at Hästlagen, near Vislanda. The peat is spread on large drying fields and the moisture reduced to 40 per cent. It is crushed and ground and further dried by passing through long passages with combustion chambers beneath. The water content is reduced to 12–15 per cent. and the material sieved and further crushed. The peat is carried on the tender of the locomotive in an air-tight tank, and is forced by air pressure to the furnace, in which a small coal fire is kept burning. The average kilograms of steam generated per kilo. of fuel are given as 4·71 kilos. (calorific value of peat, 7,740 B.Th.U.) as against 6·81 kilos. for coal (calorific value, 12,000 B.Th.U.).

Successful results have been obtained in the use of dry peat powder for steam raising in Sweden, injection by air heated to 200° F. being employed. From 1·2 to 1·4 lb. of dry peat were equivalent to 1 lb. of coal, the relative cost per ton being stated as 16*s.* 6*d.* and 9*s.* 4*d.*, but some coal is required when starting up. This method seems unlikely to find wide application.

Peat Charcoal. The denser forms of air-dried peat and peat briquettes lend themselves to gasification in retorts, for the production of peat coke and gas. Since peat has no binding properties on carbonization it must be treated in lump form if lump coke is to be obtained. Originally peat was carbonized in heaps as in charcoal manufacture, but retort systems were in use in Germany and Russia in the early part of the century. The Ziegler process (*Engineering*, Nov. 15, 1907) gives the following yields :

	Peat coke, 33 per cent. Tar, 4–5 per cent.	Semi-coke, 45–50 per cent. Tar, 2 per cent.
Carbon . . .	86–88 per cent.	74 per cent.
Hydrogen . . .	2·0	3·6
Oxygen . . .	5·2–5·5	14·5
Sulphur . . .	0·3	0·2
Calorific value . .	14,500 B.Th.U.	12,400 B.Th.U.

The by-products are of considerable importance, and the yields for a plant working 35,000 tons of air-dried peat per annum are given from two sources : (1) Zwingenberger, *Eng. and Min. Journ.*, 1907, **83**, 143 ; and (2) Captain Sankey, *Brit. Assoc.*, September, 1908, from actual results at Beuerberg, Munich.

35,000 tons air-dried peat give :

	(1)	(2)
Peat coke	11,655 tons	13,800 tons
Ammonium sulphate . . .	140 „	184 „
Calcium acetate	210 „	270 „
Methyl alcohol	70 „	92 „
Oils, heavy and light . . .	1240 „	1380 [1] „
Paraffin, solid	117 „	230 „

[1] Assuming average gravity of 0·85.

The charcoal has proved of value for carburizing armour plate, and the semi-coked peat was tried as fuel in the German Navy ; but although no data can be quoted as to its density, such fuel is unlikely, however carbonized, to prove sufficiently dense to be a useful bunker fuel.

Experiments on the production of town's gas are described in Fuel Research Technical Paper 4 (1921). Irish block peat was carbonized in Glover–West continuous vertical retorts and gave very satisfactory results as follows :

Carbonizing temperature . . .		980° C.	850° C.
Yields per ton of peat (20 per cent. H_2O)—			
Coke	cwt.	5·4	5·4
Gas	cu. ft.	14,900	13,760
„	B.Th.U.	325	340
„	therms	48·4	46·8
Tar	gals.	12·6	21·3

The peat charcoal was fairly hard and dense and made a reactive fuel ; it had a high calorific value of 12,600 B.Th.U. per lb. dry, with

10 per cent. of ash. It would find useful applications for certain metallurgical purposes.

Gasification of Peat. Great expectations have been entertained that by gasification, with recovery of perhaps 80 per cent. of the nitrogen as ammonium sulphate, a great deal of peat could be utilized, a matter of considerable importance in countries often poorly supplied with other fuels. Many large power schemes have been visualized on these lines, but the great depreciation in the value of ammonium sulphate, through extensive production synthetically, has profoundly altered the economic prospects of all such schemes.

The gasification of peat has been successfully carried out in producers (Chapter XVI) modified suitably to meet the conditions of wetness and low density of the peat as charged. The following figures are amply supported by tests made by the Power Gas Corporation and others:

	Per metric ton (dry peat substance).
Cubic feet of gas at 0° C. and 760 mm.	99,000
Calorific value per cubic foot	157 B.Th.U.
Tar	110 lb.
Calcium acetate	9 "
Ammonium sulphate	165 "

From the available results it may be confidently expected that 1 ton of dry peat substance will yield 90,000 cu. ft. or over of gas of a calorific value of 140 B.Th.U. per cubic foot.

Taking these figures as a basis, and assuming that a good gas engine will, under varying working loads and everyday running, give an efficiency of 25 per cent.; thus requiring 10,180 B.Th.U. per H.P. hour, one ton of theoretically dry peat will be equal to an output of 1240 H.P. hours, or 1·8 lb. per H.P. hour. High-class modern gas engines, working at or near full load, will require only 8500 B.Th.U. per H.P. hour, and on this basis one ton of dry peat may be expected to give 1480 H.P. hours, equal to 1·51 lb. per H.P. hour. Converted into electric energy the consumption of dry peat per kilowatt would be therefore about 2 lb.

Working with a peat containing 2·2 per cent. nitrogen, Messrs. Crossley Bros. obtained in their earlier trials 140 lb. sulphate per ton (= 63 per cent. yield), and later 177 lb. (= 80 per cent. yield).

MINOR SOLID FUELS

As these are closely allied to either wood or peat, consisting chiefly of cellulose, they may be considered here conveniently.

Bagasse (*Engineering*, 1910, **89**, 197) is a fuel of considerable importance in cane-sugar-producing countries, and consists of the residual crushed cane after the extraction of the juices. It is usually burnt under boilers, the best results being obtained when over 100 lb. per hour are burnt per square foot of grate area.

Bagasse contains:

Fibrous material (cellulose)	33–50	per cent.
Sugar	7–10	„
Water	32–56	„

Naturally the amount of fibrous material available for fuel is dependent largely on the degree to which the juices are pressed out.

The calorific value of dry bagasse ranges from 4600 cals. (8280 B.Th.U.) to 4800 cals. (8650 B.Th.U.), with an ash content of 1·6 to 2·25. The value of the pure combustible approximates very closely to 4750 cals. (8560 B.Th.U.).

Spent Tan. This will have much the same composition as wood. According to D. M. Myers (*School of Mines Quarterly*, 1910, **31**, 116), hemlock tan has the following ultimate composition:

Carbon	51·8	per cent.
Hydrogen	6·04	„
Oxygen	40·74	„
Ash	1·42	„

The calorific value of air-dried bark is 3150 cals. (5675 B.Th.U.), and of the wet tan 1480 cals. (2665 B.Th.U.), the average moisture being 65 per cent. (Myers).

Spent tan has been successfully employed in suction gas plants.

Nile Sud. Considerable attention has been given to the utilization of the enormous quantities of grass clumps which at certain seasons are carried down the Nile, it being realized that in a country dependent almost entirely on imported fuel, the application of this sud for fuel purposes is an important economic factor. The material is collected, sun-dried, disintegrated, and finally briquetted. It is claimed that, produced on the banks of the Nile, the fuel is 50 per cent. cheaper than imported fuel.

Town Refuse. The disposal of the waste material from dustbins, etc., is an important sanitary problem, and its destruction by burning in suitable "destructors" is not only a satisfactory method from a sanitary point of view, but can generally become remunerative when the heat is utilized for steam raising. As an adjunct to the ordinary boiler plant in electricity generating stations "destructors" have considerably reduced fuel consumption, and with a good type of destructor little nuisance from dust, etc., should be experienced.

Refuse varies considerably in character according to the towns, and with the season; the average amount of combustible matter for London is stated to be about 38 per cent.

The Dawes report on the public cleansing of London states that refuse collection costs about 8*s*. per ton and its disposal 9*s*. 6*d*. per ton. The nature of the London material is as follows:

	Winter.	Summer.
Fine dust	35	17
Fuel cinders	32	15
Putrescent material	9	24
Paper	10	23
Metal	3	5
Rags	1	2
Glass	2	3
Bones	2	1
Miscellaneous	7	9

The raw mixture contains from 10 to 40 per cent. of moisture and has a net calorific value of 3000–4000 B.Th.U. per lb. In the northern towns, where the refuse contains more cinders, the calorific value is higher, 4000–5000 B.Th.U. per lb.

Several types of refuse destructor have been described by E. W. Smith (*J. Inst. Fuel*, 1932, **6**, 88) who states that thermal efficiencies of over 64 per cent. on the *net* value can be obtained. The thermal losses are waste gases, 18; unburned fuel, 7, and radiation, etc., 11 per cent. A modern unit destructor will handle 30 tons of refuse per day. The material is all handled mechanically, passing over magnetic separators to remove metal, and being forcibly charged to the destructor cells which may be either of the high-pressure blast type or the rotary-kiln type. Special grates are generally necessary to dispose of the large proportion of non-combustible matter, these may be rocking or rotatable grates to keep the burning mass in motion.

CHAPTER III

COAL AND ITS CONSTITUENTS

Formation of Coal. It has long been realized that coal has been formed by the decay of plant materials accumulated millions of years ago—the presence of so many recognizable plant remains in coal is sufficient at any rate to warrant the belief. The process by which the coal has been formed and even the particular part of the vegetable matter responsible for the formation are, however, matters of considerable controversy.

It can be safely said that during the deposition of the coal measures, the sea and earth movements played very important parts. The extensive primordial forests flourished and vegetable matter accumulated either where it grew or at places such as lakes and estuaries to which it had been transported by water. These areas later became submerged owing to the changing contour of the land brought about by earth movements, etc., and the vegetation decayed, giving the first step towards coal. Later these areas were again exposed and the cycle started once more.

This alternate exposure and submersion of portions of the earth's surface led to the vegetable remains accumulating in layers, whence by the action of various agencies such as pressure and temperature coal seams resulted.

The original vegetation contained constituents with varying resistances towards decay, some such as waxes and resins being almost unaffected during the coalification process, whilst others have been transformed into materials with little resemblance to their original parent substances.

Fischer and Schrader (*Brennstoff Chem.*, 1921, **2**, 37) have suggested that during decay, bacterial action has decomposed the celluloses into gaseous and liquid products whilst the lignin has been converted into humic substances (or ulmins, i.e. brown or black colloidal substances soluble at first in alkali solutions), which in turn have been transformed into the amorphous material which constitutes the bulk of coal, the extent of the transformation determining the type of the resultant coal, a comparatively slight transformation giving rise to an immature brown coal in which the ulmins are still soluble in alkali, whilst a more extensive transformation would give rise to a more mature bituminous or anthracitic coal in which the transformed ulmins are no longer alkali-soluble. It is of interest to trace the origin of the term "ulmins." In Brande's *Manual of Chemistry* (1841) it is stated that "the peculiar brown matter which may be extracted from bog-earth, peat and turf is frequently termed 'humus' . . . there is also a brown exudation found upon the bark of trees, and especially of the elm, and hence called 'ulmin,' which contains a similar matter combined with potassa . . . by digestion with weak solutions of caustic or carbonated potassa, a brown liquid is obtained from which acid throws down 'ulmin.'"

In contradistinction to Fisher, Bode, Marcusson, Berl and others postulate the complete disappearance of the lignin and the formation of coal from cellulosic bodies. The present state of knowledge does not admit of a definite pronouncement in favour of either theory.

Whatever may be the claims of the supporters of either theory, the following facts bearing upon the origin of coal are worthy of attention. Bergius (*J.S.C.I.*, 1913, **32**, 463) found, on subjecting pure cellulose to the action of water at about 340° C., that a black substance was formed which had the composition C, 84 ; H, 5 ; O, 11 per cent. and which in some respects resembled coal; the yield is not stated.

Later (*Chem. Ztg.*, 1928, **52**, 447) he heated cellulose and wood with water to 6000 kg. per sq. cm. and obtained a "coal" containing 87 per cent. of carbon. The gases evolved were methane, hydrogen, and oxides of carbon. E. Berl and A. Schmidt (*Ann.*, 1932, **493**, 97 ; **496**, 283) have prepared artificial coals from cellulose and lignin at 150° to 350° in the presence of water and saturated salt solutions and under high pressures. They conclude that there is a fundamental difference between cellulose and lignin coals and quote the following figures:

	Cellulose coal.	Lignin coal.
Bitumen soluble in benzene . . .	15	0·5 per cent.
Coal yield	33	65 ,,
Phenols in distillation . . .	3·6	0·5 ,,

On this basis Berl and Schmidt suggest that plants rich in cellulose, but poor in lignin, resins and waxes formed bituminous coals, while plants rich in lignin formed the brown coals.

Groppe and Bode (*Braunkohle*, 1932, **31**, 277, 299, 309) have heated peat to 300° C. at 1800 atmospheres, and believe that lignin yields bright coal and cellulose tough matt coals.

Mackenzie Taylor (*Fuel*, 1926, **5**, 195; *Colliery Guardian*, 1930, **141**, 1781) has offered a novel theory that coal is the result of two types of bacterial action.

(i) Action not truly anærobic, leading to the formation of peat.

(ii) Continuous anærobic fermentation under alkaline conditions leading to the formation of bituminous coal. The alkalinity necessary for absorption of the carbon dioxide produced has been maintained by base exchange in the layer of alkaline clay which Taylor suggests covers every deposit of coal. Differences in the alkalinity of the clays have created the different types of coal recognized; lignites, where low alkalinity has limited the extent of fermentation, and bituminous coal where the roof is sodium clay of high alkalinity. This theory indicates how all types of coal can be formed without presupposing the aid of high temperatures or pressures.[1]

To illustrate the general course of the differences in types of coal Percy has constructed his well-known table (Table VIII).

TABLE VIII

TYPES OF COAL

CARBON = 100

	Hydrogen.	Oxygen.	Available hydrogen. $\left(\text{Hydrogen} - \frac{\text{Oxygen}}{8}\right)$
Cellulose, pure	13·9	111·0	0·0
Wood, average	12·0	88·0	1·0
Peat	10·0	57·0	3·0
Lignite (Khirgis Steppes)	7·8	54·0	1·1
Brown coal (Europe)	7·9	36·0	3·4
Lignite (Europe)	6·9	30·0	3·5
Bituminous coal (Staffs.)	6·0	21·0	3·4
Steam coal (Welsh)	5·0	5·5	4·3
Anthracite (Welsh)	4·75	5·2	4·1
Anthracite (Penns.)	2·8	1·8	2·6
Graphite	0·0	0·0	0·0

The regular progression of these changes is clearly illustrated in Fig. 2, given by H. G. A. Hickling (*Trans. Inst. Min. Engs.*, 1926, **72**, 261), where, until the anthracite zone is reached, the concentration of the carbon and oxygen may be represented by a straight line. The more rapid concentration in the anthracite region has not been satisfactorily explained, although it has been suggested that it is due to abnormal heating.

MACRO- AND MICRO- COMPONENTS OF COAL

Visual examination of coal in the seam or in large pieces shows that it is not homogeneous throughout its mass. With most coals

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[1] For further consideration of the processes involved in the formation of coal the reader is referred to Walcot Gibson's excellent treatise on *Coal in Great Britain* (Edward Arnold).

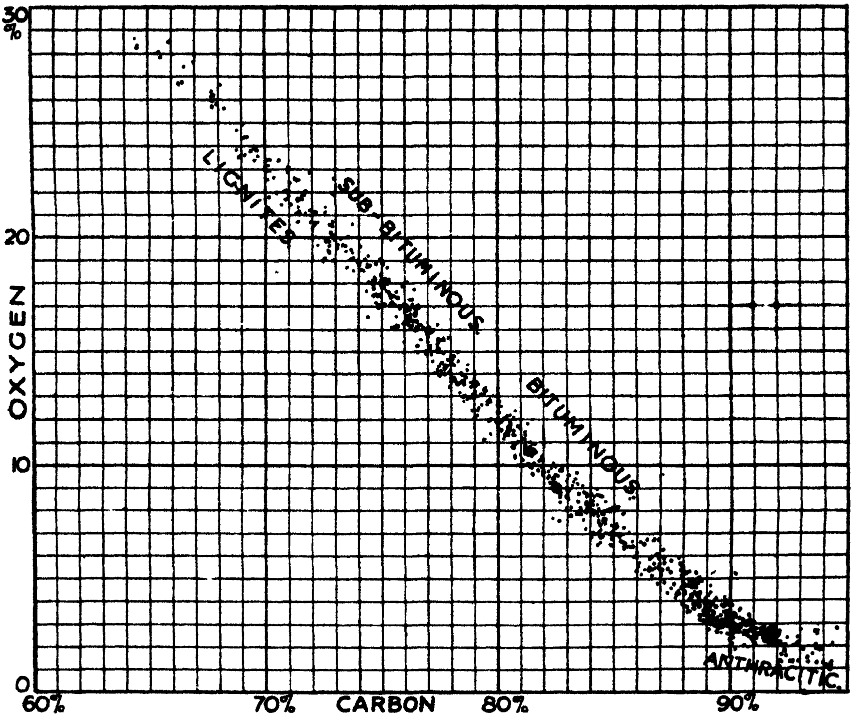


FIG. 2.—Carbon-Oxygen Content of Pure Coal Substance from Lignites to Anthracites (Hickling).

differences in texture are apparent, some bands having a dull and others a bright appearance. These bands may be separated from one another by " dirt " bands or may merge into one another without visible partings. These differences are most marked in the case of bituminous coals but can be traced in lignitous coals, in certain black lignites and, to a less extent, in carbonaceous coals. The identifiable macroscopic constituents in bituminous coal have been termed by Stopes vitrain, clarain, durain and fusain, and by Thiessen, anthraxylon (vitrain and clarain) and detritus (durain). Similar terms in German nomenclature are glanzkohle, mattkohle and faserkohle.

Vitrain. Vitrain is the bright black brittle coal which normally occurs in very thin bands. It breaks with a conchoidal fracture and, when viewed in very thin sections, is generally translucent and amber-red in colour. It is almost free from plant structures but shows a faintly defined cellular structure. A typical thin section of vitrain is shown in Plate I (*a*).

Clarain. Clarain is bright black but less bright than vitrain. It is often finely banded so that it tends to break irregularly. In thin sections it shows partly the same appearance as vitrain and partly transparent plant remains such as spore exines, cuticle and woody fragments. Plate I (*b*) shows typical clarain structure.

Durain. Durain is the dull greyish-black coal which is hard and tough and breaks irregularly. In thin sections it is fairly opaque and shows large and small spore exines and woody fragments in a matrix of opaque grains. Plate I (*c*) shows a typical durain structure with large flattened macrospores.

Fusain. Fusain is the soft black powdery material which occurs in very thin layers in the coal and at which fracture tends to occur. It shows the original cell structure of wood, though considerably deformed, and is considered to be woody fragments which have undergone a different process of decay from the rest of the coal. See Plate I (*d*).

Quite marked differences in the proportions and properties of these constituents are found in British coal seams. In five Lancashire seams the differences in proportions are shown by Sinnatt (*Trans. Inst. Min. Eng.*, 1922, **63**, 307) to be as follows:

	Vitrain.	Clarain.	Durain.	Fusain.
1	14·6	65·9	18·1	1·4
2	9·8	53·1	35·2	1·9
3	7·0	70·0	21·2	1·8
4	1·3	98·7	nil	nil
5	73·0		26·5	0·5

Differences in properties are shown by King (Preparation, Selection and Distribution of Coal, 1931) to be:

	Vitrain.	Clarain.	Durain.	Fusain.
Moisture	1·7	1·4	1·2	0·9
Volatile matter	34·6	37·6	32·2	19·1
Ash	0·6	3·5	4·6	9·6
Carbon.	84·4	82·2	85·8	88·7
Hydrogen	5·4	5·7	5·3	4·0
Sulphur	1·0	2·3	0·9	1·0
Nitrogen	1·5	1·9	1·4	0·7
Oxygen	7·7	7·9	6·6	5·6
B.Th.U. per lb. (dry, ash-free) .	14,790	14,790	15,100	14,840

On carbonization the vitrain gave a grey, slightly swollen coke, the clarain a similar but more swollen coke, the durain a dull-black friable coke and the fusain a pulverulent residue.

Resins. Different woods vary rather widely in their resin content, conifers, for example, being rich. Since resins are resistant to decay they are frequently found as such in coal. In certain lignites and brown coals fragments can readily be separated by hand. In bituminous coals the resinous bodies are normally of microscopic size and can be seen in thin sections as spherical or oval globules of a yellow-red colour. Occasionally it is possible to pick out small fragments of resin.

Spores. It appears certain that the bulk of the plants from which coal was formed were propagated by means of spores, some large (macrospores) and others of microscopic dimensions (microspores). During the process of decay the contents of these spores have disappeared, but the resistant cuticle has survived and can be seen in microsections (Plate I *c*). In transverse section these spore exines appear as flattened double-walled discs having been compressed during the consolidation of the matrix, but in sections along the bedding planes they are nearly circular.

INORGANIC CONSTITUENTS

The inorganic constituents of coal can be seen in part as (i) thin dirt partings separating the coal and layers and forming lines of weakness at which lump coal breaks readily ; (ii) lump pyrites in the form of dull gold nodules ; (iii) disseminated pyrites in the form of glistening scales ; (iv) white " ankeritic " partings, usually perpendicular to the bedding plane of the coal and the coal bands, consisting mostly of calcium magnesium carbonates deposited by infiltration in the shrinkage cracks in the coal substance. The distribution of these inorganic constituents and of those not visible to the eye can be seen clearly in an X-ray photograph (Plate II). The British pioneer work in this field has been carried out by C. N. Kemp (*Trans. Inst. Min. Eng.*, 1929, **177** (**2**), 175), to whom this photograph is due. Even in those parts of the coal which are most free from inorganic constituents the ash content is 2–3 per cent. The variations in distribution generally follow the horizontal coal bands, but the presence of constituents of high atomic number in the shrinkage cracks is particularly noticeable. These are the so-called ankerites. With the exception of the pyritic section, which shows 11·3 per cent. of ash, the whole of this inorganic matter shown would be regarded as inherent and not adventitious (see Chap. IV).

THE CHEMICAL CONSTITUTION OF COAL

Researches conducted in order to elucidate the problem of the constitution of coal have followed three main lines :

(i) Decomposition of the coal by the application of heat following by chemical examination of the products.

(ii) Separation of the coal into fractions by the action of solvents and their separate chemical examination.

(iii) Degradation of the coal by the controlled action of chemical reagents and subsequent examination of the products.

Action of Heat. *In this field much of the work has a double significance, coal constitution on the one hand and carbonization on* the other. There is no clear distinction between the search for knowledge as regards the constitution of coal and investigations relating to its coking properties. When coal is heated it gives as volatile products tar, liquor and gas, and as a residual product coke, which may be weak and friable or hard and cellular according to the nature of the coal. The composition and nature of these products vary with the temperature, the pressure, the rate of heating and the nature of the coal.

The thermal decomposition of coal has been the subject of close investigation over a considerable period, chiefly by Wheeler and his collaborators.[1] It has been established that when a bituminous coal is heated there is first evolved the occluded gases, composed mainly of higher paraffin hydrocarbons, followed by substantial amounts of water at about 200° C. Thereafter appear at intervals sulphuretted hydrogen and olefines (270°), oils unaccompanied by marked gas evolution (310°), and finally, commencing at about 350°, a continuous gas evolution together with much viscous oil. The nature of the evolved gas alters as the heating progresses. Below 450° it largely consists of paraffin hydrocarbons, but these cease to be evolved at temperatures above 700°, whilst this latter temperature marks a sudden rapid increase in the quantity of hydrogen evolved.

The composition of the tar evolved below 450° has been studied by both Wheeler and Pictet[2] and their respective collaborators, who have ascertained the presence of large amounts of naphthenes and unsaturated hydrocarbons together with smaller quantities of phenols and aromatic hydrocarbons, and very small quantities of bases.

That the above facts are substantially correct is shown by their independent confirmation by other workers, amongst whom may be mentioned Porter and Taylor, but the "explanation" of these facts has led to considerable controversy; the foundations upon which theories have been built have been shown by more mature thought and work to be insecure. Nevertheless, it should be possible, if our knowledge were adequate, to trace the connection between the products of thermal degradation and the constituents of coal. This has recently been attempted by Holroyd and Wheeler (*Fuel*, 1930, **9**, 40, 76, 104), who examined the products obtained by the distillation of several coals in a high vacuum, thereby largely avoiding secondary decomposition. Their results are summarized in the following table (IX):

[1] Burgess and Wheeler, *J.C.S.*, 1910, **97**, 1917; 1911, **99**, 649; 1914, **105**, 131. Clark and Wheeler, *J.C.S.*, 1913, **103**, 1704. Jones and Wheeler, *J.C.S.*, 1914, **105**, 141, 2562; 1915, **107**, 1318; 1916, **109**, 708.

[2] Pictet, etc., *Comp. Rend.*, 1913, **157**, 1436; 1915, **160**, 629. *Ber.*, 1915, **48**, 926.

TABLE IX

Resolution of Bituminous Coals by Heat

(Holroyd and Wheeler)

Constituent.	Principal Gaseous Products.	Principal Liquid Products.		
		Character.	Quantity.	Temperature Range, deg. C.
Free hydrocarbons.	Paraffins in small quantity.	Saturated and unsaturated hydrocarbons in nearly equal amount.	Equal to original amount of free hydrocarbons in the coal.	225–300.
Resins . .	Paraffins and higher olefines.	Resins and unsaturated hydrocarbons.	Usually rather less than original amount of resin in the coal.	325–375.
Structured Plant Entities (e.g. spore exines).	Oxides of carbon and some paraffins.	Unsaturated hydrocarbons, neutral oxygenated compounds and water.	About 30 per cent. of original plant entities in the coal.	300–320.
Ulmins .	Paraffins and some oxides of carbon.	Phenolic and acid oils, unsaturated hydrocarbons, aromatic and hydro-aromatic compounds and water.	Decreases with the "rank" of the ulmin 6·1 per cent. of water and 3–0·05 per cent. phenols with coals ranging from 77–90 per cent. carbon.	Decomposition point increases with "rank" of ulmin from 290–365 with coals ranging from 77–90 per cent. carbon. All oils distilled below 400.

The constituents mentioned in the table were also distilled separately, when it was found that the hydrocarbons could be distilled unchanged, the resins decomposed partially *in vacuo* at 200–300°, and the organized plant remains above 300°. The ulmins decomposed at definite temperatures depending on the rank of the coal. It seems probable that the hydrocarbons either exist as such in coal, or are loosely attached to the complex ulmin molecule.

Recently some work has been carried out on the thermal decomposition of coal in a very high vacuum. Stone and Travers (*J.S.C.I.*, 1933, **52**, 686) have used pressures of 0·01 and 0·001 mm. Hg., and state that the yield of distillate at 350° C. approaches the amount of extract obtained by Bone (see later) with benzene under pressure. Moreover, the distillate consisted of a soft reddish-brown pitch almost completely soluble in benzene, and of liquid and gaseous hydrocarbons. The formation of carbon dioxide and hydrogen sulphide shows that some decomposition had taken place at this temperature even under such low pressures.

Juettner and Howard (*J.A.C.S.*, 1933, read Sept. 11) employed an evaporative still under pressures of 0·01–0·001 mm. Hg. at temperatures up to 525° C. They concluded, since condensible products could not be obtained, even under the most favourable conditions, until the temperature was such that gas evolution was considerable, that any chemical entities which may be present in coal cannot be distilled in experimental time owing to their low vapour pressure.

It will be seen that research on the thermal treatment of coal has added little to our knowledge of the constitution of coal. The amount of distillate is small in comparison with the amount of residue, and moreover, the nature of the products is so complex that little has been discovered about them. The work done has, however, served a useful purpose in supplying information of value to the carbonization industries, and has thrown light on the relationship between low- and high-temperature tars.

Solvent Extraction. At first sight it would appear that solvent extraction of coal must be a promising line of attack; this probably explains the fact that a very large number of solvents have been tried upon coal. Very few of these have, however, given results of any real value and only on one or two have extensive researches been made. These are benzene (under pressure) and pyridine and perhaps certain binary mixtures.

Benzene under pressure has been used by Fischer and his collaborators in Germany and later in this country by Bone and others.

Fischer heats the coal in an autoclave in contact with benzene at 205° C. for one hour, and repeats the procedure with fresh solvent until no more extract is obtained. The concentrated extract is poured into 3–4 times its own volume of light petroleum (b.p. 40–60°) and the precipitate of " solid bitumen " filtered off, the filtrate being evaporated to give a residue of " oily bitumen." Bone's procedure is to extract the coal in an autoclave of the Soxhlet type, in an inert atmosphere. The extract is concentrated and poured into five times its own volume of light petroleum (b.p. 40–60°) and filtered.

The filtrate is evaporated to give the oily bitumen, but this is fractionated to give Fraction I*a*, I*b* and II.

Fraction I*a*, volatile in steam, soluble in light petroleum.
Fraction I*b*, not volatile in steam, soluble in light petroleum.

Fraction II, insoluble in light petroleum, soluble in a 1 : 4 mixture of benzene and light petroleum.

The precipitated solid bitumen is extracted with absolute ethyl alcohol to give:

Fraction III, soluble in ethyl alcohol.

Fraction IV, insoluble in ethyl alcohol.

These fractions are described by Bone (*Proc. Roy. Soc.*, 1928, **120A**, 523 and *J.S.C.I.*, 1931, **50**, 407) as follows:

Fraction I. A yellow-brown, viscous, non-nitrogenous neutral oil of vaseline-like consistency with a C/H ratio less than 10 and low oxygen content.

Fraction Ia has a higher oxygen content than *Fraction Ib*, and the latter may be regarded as an unchanged constituent of the coal.

Fraction II. A reddish-brown solid with a softening point below 60° C. and a C/H ratio about 13.

Fraction III. A non-nitrogenous, reddish-brown, brittle, resinous solid, usually softening below 150° C. and having a C/H ratio of about 12·5.

Fraction IV. A neutral, amorphous cinnamon-brown nitrogenous powder, softening only at temperatures above 150°, usually between 150° and 250° C., undoubtedly of a benzenoid nature and with C/H ratio about 15·0.

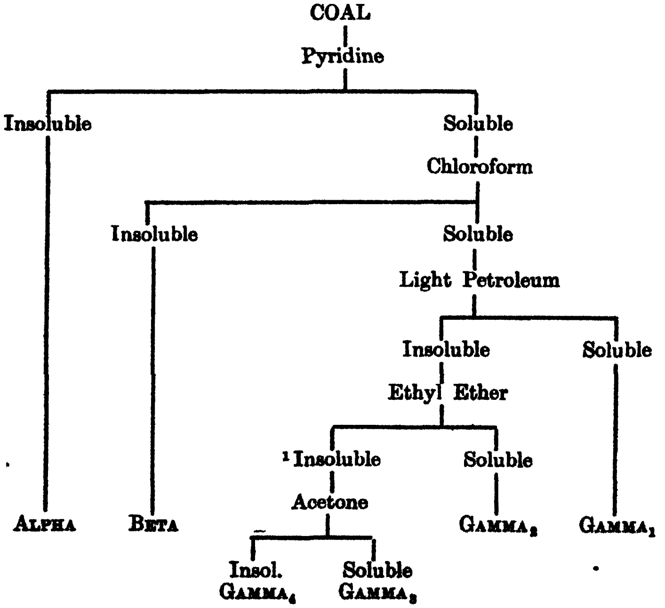
Bone regards Fraction II as being probably a mixture, while Fractions I*a*, I*b*, III and IV are each composed of a single type of chemically distinct substance. There is, however, considerable doubt about this.

The important observation has been made that no matter what type of coal is employed for the extraction with benzene under pressure, the insoluble residue is always entirely devoid of any coking propensity. It is natural, therefore, to try to relate the coking power of a coal to the benzene extract or specific portions thereof. Unfortunately the two schools have advanced conflicting opinions and at present there is no adequate explanation of this divergence. Fischer claims that the "oily bitumen" (Bone's Fractions I and II) is mainly responsible for the caking property of a coal while the swelling is due to the "solid bitumen" (Bone's Fractions III and IV), and has published photographs in support of his claim. Bone, on the other hand, contends that Fraction I makes no contribution to the coking propensity of a coal, Fraction II may or may not, but Fractions III and IV are mainly responsible for the coking property, although the contribution by Fraction III is inappreciable because the amounts of this fraction are small. In fact, the relative agglutinating powers of a series of bituminous coals run nearly parallel to their yields of Fraction IV.

It is not held that the coking property is *entirely* due to the presence in the coal of certain substances, but, in addition, other factors operate, which circumstance may account for the conflicting results.

More recently Fischer, Peters and W. Cremer (*Brennstoff Chem.*, 1932, **13**, 364) have shown that the amount of extract obtainable with benzene and other solvents at their boiling-point can be increased more than 10 times by grinding to μ size (0·001 mm.). The increase is sudden. Reduction of particle size makes no difference until particles of the order of 10μ are reached. The increase in extract between 10μ and 1μ is not proportional to the increase in surface, and Fischer and his colleagues have suggested that the solvent can only affect a surface layer, which in view of the sudden increase of extract with particles of size 1μ, must be of a thickness of the order of one-half μ.

The action of pyridine as a solvent for coal has been investigated exhaustively, principally by Wheeler and his collaborators. The yield of extract obtainable from a bituminous coal, provided the solvent is pure and anhydrous and that the extraction is carried out in an inert atmosphere, amounts to 20 to 25 per cent. on an average, as against 7 to 15 per cent. for benzene under pressure. The pyridine extract is further fractionated with other solvents, the method being shown diagrammatically:



The *beta fraction* is generally regarded as being similar in type to the *alpha fraction*, and Wheeler suggests that it consists of dispersible ulmins whilst the alpha fraction consists of undispersible ulmins of higher molecular weight. This is supported by Mahadevan (*Fuel*, 1929, **8**, 462), who examined these fractions by the X-ray diffraction method.

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[1] Since the original publication appeared the procedure has been curtailed and the fractionation stopped at this point. This insoluble residue is now termed Gamma$_3$.

The gamma fractions are regarded as being the hydrocarbons and resins present originally in the coal; and are described by Cockram and Wheeler (*J.C.S.*, 1927, 700; 1931, 854) as follows:

Gamma$_1$ was of vaseline-like consistency, and was found to consist of—

(*a*) Saturated hydrocarbons, 40 per cent., containing C, 87·40; H, 11·13 per cent. These contained hydrocarbons of other than straight or branched chain structure.

(*b*) Unsaturated hydrocarbons, 40 per cent.

(*c*) Resins (dark red in colour), 20 per cent., containing C, 84·21; H, 7·31 per cent.

Gamma$_2$ was a brick-red powder, m.p. 100–110° C, containing 15 per cent. of saponifiable matter consisting of phenols and carboxylic acids (as esters), some of which contained hydroxyl groups. The unsaponifiable portion, m.p. 90–100° C., resembled the resin from Gamma$_1$. Its composition was $C = 84{\cdot}0$; $H : 7{\cdot}2$; $O = 8{\cdot}8$ per cent. Nitrogen and sulphur were absent. No carboxylic, ketonic, aldehydic, or alcoholic group was present, and the oxygen was probably present as non-reactive bridge linkages.

Gamma$_3$, *Gamma*$_4$ were brown powders similar in composition and general properties, being insoluble in alcoholic potash.

Cockram and Wheeler (*loc. cit.*) found that hard well-fused cokes were produced from mixtures of alpha and beta with gamma$_1$ and gamma$_2$ but not with gamma$_3$.

Hoffmann and Damm (*Brenn. Chem.*, 1922, **3**, 73, 81; 1923, **4**, 65) examined the neutral oil obtained from the pyridine extract of an Upper Silesian coal, and isolated a number of paraffins (including heptacosane), saturated and unsaturated hydrocarbons and also methyl anthracene. The identification rested on physical properties and is therefore not entirely satisfactory.

Of the other solvents which have been employed mention may be made of tetralin, used by Novák and Hubàček (*Paliva à Topeni*, 1927, **9**, 165, 187; 1928, **10**, 3, 22, 28, 41), and of mixed solvents used by Szilard and Istvan (*Szén-Közle*, 1927, **2**, 45). With regard to mixed solvents it was found that 50 : 50 mixtures of benzene and alcohol gave higher yields of extract than either solvent alone. A paper by Ashmore and Wheeler (*J.C.S.*, 1933, 1405) draws attention to the fact that in some cases the use of mixed solvents leads to the formation of condensation products which are included in the extract.

For further details concerning these solvents reference should be made to the comprehensive paper by Bakes (Fuel Research Tech. Paper No. 38), which contains an excellent literature summary and also an account of an attempted correlation between pyridine and benzene-pressure extractions.

From the account that has been given of the action of solvents on coal it is obvious that the amount of real knowledge gained about the structure of coal, while greater than that afforded by a study of the action of heat, is still only slight.

Chemical Degradation. The greatest insight into the constitution of coal has been gained from the examination of the chemical degradation products of coal or natural or regenerated ulmins. It will be readily understood that chemical degradation leads necessarily to the formation of substances less complex in type than those originally present in the coal so that the characterization of degradation products can only give information of the presence of structural units with which the complex coal structure has been built and can give little or no information concerning the complexity of the structure. Nevertheless, a knowledge of the building units is important from many aspects, not the least of which may be the more scientific utilization of our coal resources.

Although a great variety of reagents has been employed in the attack on coal, yet only in a very few instances has the examination of the products been prosecuted with any thoroughness, and even in some of these cases assertions have been made on very meagre evidence concerning the identity of certain constituents. Of the many methods employed oxidation has proved to be the most useful.

The products of decay, the ulmins, of the various plant entities which have taken part in the formation of coal are at first soluble in alkali, but as the age of the deposit increases, further changes take place in the character of the ulmins until they become devoid of any acidic character, and in their place appears the amorphous material, insoluble in alkali, which constitutes the bulk of any bituminous coal. It is considered by Francis and Wheeler (*J.C.S.*, 1925, **127**, 112) that the original alkali-soluble ulmins (present in peat and brown coal) and the insoluble ulmins of a bituminous coal have the same nuclear structure but differ in their external groupings. Whatever may be the truth of this assertion, it is a fact that mild oxidation, say with air, largely transforms a bituminous coal into alkali-soluble material closely resembling alkali-soluble ulmins. This procedure has been called by Francis and Wheeler " regeneration " of the ulmins. These authors have shown that vitrain can be oxidized with air at 150° C. and rendered soluble in dilute caustic alkali to the extent of 97 per cent. of the coal substance. The ulmins, natural and regenerated, are readily recovered from solution in alkali by precipitation with mineral acid and washing free from electrolyte.

From considerations of the nitrogen and hydroxyl content and equivalent of regenerated ulmins these same authors (S.M.R.B. Tech. Paper No. 28) conclude the molecular weight to be 680 or some multiple thereof, each unit of 680 containing one nitrogen atom, one hydroxyl and four carboxyl groups. The further oxidation of the regenerated ulmins with hydrogen peroxide gave rise to oxalic, succinic and probably benzene-carboxylic acids, whilst the use of nitric acid (30 per cent.) gave 4 : 6-dinitroresorcinol and acetic, picric and mellophanic (1 : 2 : 3 : 5 benzene tetracarboxylic) acids.

The chemical properties of humic acids (i.e. natural alkali-soluble ulmins) vary according to their source and have been closely investigated by Fuchs. He considers the reaction product with dilute nitric acid, the so-called nitrohumic acid, to be an isonitroso-tetracarboxytrihydroxy compound, whilst for the completely methylated "nitrohumic acid" from Kassel brown coal he proposes the formula $C_{59}\ H_{36}\ O_{17}\ (COO\ CH_3)_4\ (O\ CH_3)_3\ (CO.C{:}NOH)$ with a molecular weight of 1200–1400.

Sven Oden has shown that alkali-soluble peat ulmins contain four carboxyl groups per molecule and has suggested the formula $C_{60}\ H_{52}\ O_{24}\ (COOH)_4$. In view of the uncertainty of the ulmins being chemical individuals, such conclusions should be accepted with reserve.

Tropsch and Schellenburg (*Ges. Abh. z. Kannt. der Kohle*, 1921, **6**, 196) have examined the fusion products of humic acids with caustic alkali and have found small quantities of formic, acetic, oxalic, isophthalic, *m*-hydroxybenzoic and hydroxyisophthalic (1 : 3 : 5) acids. The same authors (*loc. cit.*, p. 214) oxidized humic acids with nitric acid and isolated a trinitrodihydroxybenzene of unknown constitution.

Recently Fischer, Peters and Cremer (*Brenn. Chem.*, 1923, **14**, 184) have investigated the slow oxidation in a current of air of μ coal (i.e. of particle size of the order of 1 μ = 0·001 mm.) and have obtained a crystalline sublimate containing phthalic acid.

Fischer and Schrader have oxidized coal with air by heating with alkali under pressure and have obtained formic, acetic, succinic and various benzene carboxylic acids including benzoic acid.

An important contribution to our knowledge of the constitution of coal has been furnished by the work of Bone, Horton and Ward (*Proc. Roy. Soc.*, 1930 [A], **127**, 480), in which the insoluble residues from the pressure-benzene-extraction of various types of coal were oxidized with boiling alkaline potassium permanganate solution. It was shown that all types of coal from a brown to a well-matured coking coal gave appreciable yields of acetic and oxalic acids and from 33 to 50 per cent. of the original coal substance as benzene carboxylic acids. It was thus inferred that a considerable part of the original coal substance had a "benzenoid" structure.

CHAPTER IV

COMPOSITION AND CLASSIFICATION OF COAL

It was pointed out at the commencement of Chapter III that coal as mined consists of the coal substance itself associated with certain inorganic constituents and with variable amounts of free dirt. In order to compare types of coal one must consider the coal substance only, but in assessing the value of the coal for certain purposes it is necessary also to include the amount and properties of the inorganic constituents which form ash on combustion. There are also certain minor constituents which are not included in comparing types of coal but whose presence and amount may limit the uses to which a coal can be put.

This chapter deals not only with the comparison of types of coal, i.e. classification, but also with the effect of the different constituents such as moisture, ash, etc., which are not dealt with in Chapter III.

Moisture in Coal. The moisture in coal may be divided into accidental or " free " moisture, and the moisture due to the hygroscopic properties of the coal itself. Thus an oven-dried coal will again absorb moisture up to a certain limit, or a wet coal exposed to the air will lose water down to a certain limit. Lignites and brown coals frequently contain from 30 to 45 per cent. of moisture as mined, and, even in summer, on exposure to air retain frequently 20 per cent., in this respect resembling wood. Bituminous coals may contain from 1 to 12 per cent. after air-drying. The moisture retained by the coal on air-drying is sometimes called " inherent " moisture.

High moisture is, of course, prejudicial to the buyer: it is paid for and transported at fuel prices, it adversely affects the coal in the furnace by chilling the fire, so giving greater chances for smoke to form, and it demands heat for its vaporization. This latter loss seldom needs to be taken into account, for even under poor conditions of flue gas temperature it approximately amounts to 0·1 per cent. of the total calorific value for each per cent. of moisture.

A certain minimum of " free " moisture is of advantage in boiler-firing, about 5 per cent. giving optimum results for thermal efficiency. Similarly, in the coking of coal the best results are obtained with charges containing 3 to 5 per cent. of free moisture. The presence of moisture cannot, therefore, be condemned out of hand.

The amount of moisture which a coal retains on air-drying in the laboratory can be taken roughly as a measure of rank. High-oxygen coals retain high percentages of moisture; the non-caking coals of Leicestershire retain 8 to 10 per cent. of moisture. Low-oxygen coals retain low percentages of moisture; the coking coals of Durham retain only 1 to 2 per cent. of moisture as also do the Welsh steam coals and anthracites.

"Ash" in Coal. The mineral matter in coal is derived in part from that present in the original vegetable substance (inherent), in part from material carried by flood water, etc., amongst the decaying vegetable matter, and may also be due partly to shale, etc., derived from the strata adjacent to the coal seam, which it has been impracticable to remove by picking or washing, even where this has been attempted (extraneous). The mineral matter in coal is generally termed "ash" since it is measured by the inorganic residue remaining after "ashing" the coal completely.

"Ash" is inert material in the coal; it is valueless mineral matter paid for at coal prices. An excess of ash may detract seriously from the value of the coal by restricting the air passage through the grate, thus lowering the rate of combustion and the output of the boiler; frequent cleaning of the fires is necessary with the accompanying losses through open fire doors; the loss of carbon carried through into the ash pit may be considerable; it causes deposits in tubes and flues, and in addition, if of a fusible character, is especially troublesome through the formation of clinker. In boiler plants using powdered coal the ash generally necessitates the provision of special plant to trap the dust and grit. In producer gas practice fusibility is a serious question, and coals otherwise suitable may be unworkable except with such excessive steam supply that the efficiency is adversely affected. In chain-grate stokers a certain amount of ash is desirable in order that the back-end of the grate will remain covered and not allow the formation of air-holes.

The ash of coal is seldom under 1 or 2 per cent.; up to 5 per cent. quite usually in good coals, and not infrequently it amounts to over 10 per cent. According to Lessing (*J.S.C.I.*, 1925, 277 T) Clarain and Vitrain are relatively free from mineral matter, giving usually but little over 1 per cent. of ash and this is almost entirely "inherent" ash, light and powdery, with a good percentage soluble in water.

Durain has a much higher content, which is finely divided "extraneous" mineral matter, being clayey material mechanically carried amongst the decaying mass of vegetation. The ash of fusain

Lessing ascribes to the infiltration of hard and sometimes ferruginous water.

Often well-defined " cleats " or " partings " are found, with a thin scale of white or brownish mineral matter, termed " ankerites," and these have been formed from the infiltration of hard waters, and consist of carbonates and sulphates of lime, magnesia and iron.

Finely divided " inherent " mineral matter, whether from the plants or muds, cannot be removed by mechanical methods, washing, etc., but the higher specific gravity of undispersed shale, pyrites, etc., enables washing to be successfully carried out.

The determination of the amount of ash involves burning off all the combustible matter from the coal. Consequently this will simultaneously involve decomposition of such components as carbonates, the oxidation of pyrites and the driving off of constitutional water from shale. It may be that the determined ash figure is several per cent. lower than the true mineral matter content of the coal. Further, with carbonates present, the results for organic carbon in the ultimate analysis will be too high. A formula for the calculation of mineral matter from the ash percentage is given on page 55.

With coal from a given seam, the amount of ash is usually highest in the smaller sizes, due to the easy separation of pure lump coal and the consequent concentration of mineral matter in the fines.

Where the coal in the seam is hard and the dirt is friable the above is true. In some cases the coal is friable and the dirt hard, when the increase of ash with decreasing size may not be so marked or may even be reversed. The hard coals of Nottingham, Lancashire, Staffordshire, Cumberland and Scotland show this segregation, but the softer coals of Durham, Kent and Yorkshire (partly) are more variable. Chapman and Mott (*The Cleaning of Coal*) quote the following ash contents for sizes of Yorkshire coals :

Size (in.).	Over 1.	1–½.	½–⅛.	⅛–1/25.	1/25.	Average.
Silkstone	6·4	8·1	14·4	21·5	11·8	14·3
High Hazel . . .	1·8	5·6	9·0	15·7	20·8	7·2

and for one Durham coal.

Size (in.).	Over 1.	1–½.	½–¼.	¼–⅛.	⅛–1/16.	< 1/16.
Ash per cent. . .	4·8	18·6	19·5	19·5	15·6	15·8

With infusible ash, the value of two coals of similar character will be fairly proportional to their relative ash content, but it is quite otherwise if one gives a fusible and the other an infusible ash. A low ash content of a fusible character may be far more detrimental than a high ash of infusible character.

Essentially the mineral matter consists of silicate of alumina together with the basic oxides lime (CaO), magnesia (MgO), and iron (Fe_2O_3), together with traces of sulphates, carbonates and phosphates. Wood ashes are characterized by the presence of high proportions of alkalies, potash (K_2O), and soda (Na_2O), in combination with carbonic acid with little or no alumina. Peat ash contains a high percentage of lime and a little alumina. Coal ash is characterized largely, then, by the high percentage of alumina which is present. It may be noted that alumina as a constituent occurs in any quantity only in those plants existing to-day which are allied to those of the coal formations. Silicate of alumina (clay), however, would be the principal substance carried amongst the decaying vegetable matter when in a partially submerged state, judging by the usual shale beds accompanying the coal seams.

The composition of coal ashes varies widely; the following are quoted by King and Crossley (Fuel Research Tech. Paper 28, 1933) as normal limits relating to British and American coals:

Constituent.	Per cent. of ash. American.	 British.
Silica	40–60	25–40
Alumina	20–35	20–40
Ferric oxide	5–25	0–30
Calcium oxide	1–15	1–10
Magnesium oxide	0·5–4	0·5–5
Titanium oxide	0·3–3	0–3
Alkalies	1–4	1–6
Sulphur trioxide	—	1–12

Whilst it is difficult to correlate composition of the ash with clinkering property, it is certain that the nearer the composition approaches that of aluminium silicate ($Al_2O_3.2SiO_2$; $Al_2O_3 = 45{\cdot}8$ per cent., $SiO_2 = 54{\cdot}2$ per cent.), the more infusible it will be; that on replacement of part of the alumina by other bases, such as lime and magnesia, and more particularly iron oxide, the more easily fusible will it become, due to the formation of double silicates, which are far more fusible than the simple ones.

The following results are selected from a paper on the fusion temperature of coal ash by King, Blackie and Millott (Fuel Research Tech. Paper 23, 1929).

Constituents.	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	CaO	MgO	K_2O Na_2O	SO_3
1. Lancashire coal. .	27·1	0·9	23·2	29·2	0·1	7·1	2·7	3·2	7·3
2. Yorkshire coal . .	49·2	1·2	35·9	3·5	—	2·7	0·7	5·0	2·1
3. Durham coal . .	48·9	1·4	38·8	2·1	—	4·9	0·6	2·1	2·1
4. S. Staffs coal . .	47·3	1·3	38·2	1·1	—	6·3	0·8	1·3	3·6
5. Scottish coal . .	48·3	2·8	31·8	9·3	—	1·9	2·1	2·5	1·5
6. Anthracite . . .	37·4	1·8	31·9	19·7	—	3·7	1·7	1·6	2·5

Fusion Temperature ° C.		1	2	3	4	5	6
Oxidizing atmosphere	a .	1220	—	—	—	—	1315
	b .	1310	—	—	—	—	1340
Reducing ,,	a .	1115	1520	1550	1550	1430	1215
	b .	1155	1555	1605	1600	1470	1285

(*a*) Temperature of softening. (*b*) Temperature of fusion.

Fieldner and Selvig have classified ashes as follows :

Refractory	soften above 2600° F.	(1427° C.)
Medium	,, 2200–2600° F.	(1204–1427° C.)
Fusible	,, below 2200° F.	(1204° C.)

The colour of the ash is some indication of its fusibility since red ashes show the presence of an excess of iron oxide. Some white ashes may be fusible if they are high in lime ; such ashes show a high sulphate content, e.g. No. 1 above.

The use of catalysts in the hydrogenation of coal has directed attention to the rarer constituents of coal ash. It has been found that most ashes contain appreciable amounts of boron, chromium, molybdenum and vanadium, whilst in some notable quantities of germanium, tin and zinc have been found. The presence of some of these elements may prove to be of some importance.

Oxygen in Coal. The amount of oxygen in coal has an important bearing upon its properties and, as will be shown later, can be used in coal classification systems. Regarding coal solely as a fuel, oxygen is more undesirable as a constituent than moisture or ash ; an increase of 1 per cent. in oxygen content reduces the calorific value of a bituminous coal by about 1·7 per cent. Increase of oxygen content in bituminous coals is also associated with decrease of coking power and increase of moisture content ; high oxygen coals are non-coking and hold over 10 per cent. of moisture even when air-dried ; low-oxygen bituminous coals are strongly coking and hold only 1 to 2 per cent. of moisture when air-dried.

Nitrogen in Coal. It is unusual to find less than 1 per cent. of nitrogen in the coals of this country or more than 2·5 per cent.; indeed, it is exceptional to find a coal giving a higher figure than 2 per cent.

When coal is distilled or carbonized about 15 per cent. of the nitrogen is converted into ammonia together with small amounts of cyanogen and pyridine bases. More than 50 per cent. normally remains in the coke. When ammonia recovery from carbonization processes was of economic importance the percentage of nitrogen in the coal used was also important. Now that most of the industrial ammonia is made synthetically the nitrogen content of coal is not of particular significance.

Sulphur in Coal. This element is found to about the same extent as nitrogen, viz. 0·5 to 2·5 per cent. It occurs in three forms: in pyrites in combination with iron as FeS_2, which on heating under oxidizing conditions becomes iron oxide (Fe_2O_3) with liberation of sulphur dioxide; as organic sulphur compounds, from which the sulphur compounds in tar and gas are mainly derived; as sulphates, principally calcium sulphate ($CaSO_4$), forming a constituent of the ash. In some cases it is desirable to distinguish between the fixed sulphur (occurring in the coke) and volatile sulphur.

Sulphur is of great importance in fuels, especially those used for metallurgical purposes, since it may pass into the metal under treatment. Pyrites loses part of its sulphur by distillation on strongly heating, hence, when raw coal containing pyrites is burnt part of the sulphur set free may be absorbed by the grate bars, and since the sulphide of iron formed is comparatively fusible, may give rise to serious trouble, whilst, if the sulphur be burnt to sulphur dioxide, serious corrosion of copper tubes, etc., with which the gases come in contact may occur.

When coal containing sulphur is distilled in retorts or coke ovens the sulphur found in the coke is always somewhat less than in the coal, the actual loss probably being dependent mainly on the organic sulphur compounds present. Pyrites also may lose some of its sulphur, becoming iron mono-sulphide (FeS), and calcium sulphate may be reduced by contact with the hot carbon to the sulphide. In the majority of cases the coke will still contain over 80 per cent. of the original sulphur of the coal, and this residual sulphur may not be as objectionable in its altered condition of combination. It is quite conceivable that pyrites gives off elementary sulphur vapour which is readily absorbed by iron or other metal, but that iron sulphide loses sulphur only as the dioxide which may have little effect on the metal.

Numerous processes have been proposed for the further reduction of the sulphur left in the coke, but the most satisfactory method is that of washing the crushed coal, when a fair proportion of the pyrites may be mechanically separated.

Iron pyrites has been credited with the main responsibility for the spontaneous ignition of coal, but little importance is now attached to this theory. The question is fully discussed later.

Some discussion has arisen as to whether sulphur present in pyrites should be regarded as a heat-giving constituent in fuels, an important consideration when the calorific value is calculated from the elementary composition. Whilst calcium sulphate cannot undergo combustion, sulphur in organic combination and as pyrites may do so and add to the calorific value. Lord (*Trans. Amer. Inst. Min. Eng.*, 1897, **27**, p. 960) investigated the question, and concluded that practically the iron and sulphur give nearly the same heat as when burned in the free condition, and therefore the calorific effect of sulphur should find a place in formulæ used in such calculations.

Arsenic and Phosphorus. Arsenic and phosphorus occur in small quantities in most solid fuels, the former probably as arsenical pyrites. Their presence has no significance when the fuel is used for steam-raising or gas making, but in process work as, for example, the metallurgical use of coke, even small quantities can have a very undesirable effect on the product. A. Bayet and A. Slosse (*C.R.*, 1919, **168**, 704–706; *J. Soc. Chem. Ind.*, 1919, **38**, 336 A) suggested that the illness of certain persons engaged in Continental industries connected with coal was probably chronic arsenical poisoning, due to the presence of arsenical pyrites in coal. During the inquiry into arsenical poisoning from beer (Royal Commission, 1901–03) it became known that malt had, on occasions, been dangerously contaminated with arsenic from the fuel used in the kiln, also, of the various types of fuel examined gas coke appeared to be the least desirable. Since that period interest has abated, and there has been very little published information of the distribution of arsenic in fuels. Hence, many of the published figures available are probably not representative, their use at the time of publication being solely to establish the dangerous or innocuous nature of the fuel concerned in malting practice:

	Grains Arsenic per lb. of fuel.	
Coal	0·21 to 2·9	(Chapman, Moon, Daubrée)
Anthracite	nil to 0·13	(Wood, Smith and Jenks)
Gas Coke	nil to 0·52	(Wood, Smith and Jenks)
Lignite	nil to 14·0	(Daubrée)

Chapman, *Analyst*, 1901, **26**, 253; Moon, *J. Gas Ltg.*, 1901, **77**, 1061; Daubrée, *C.R.*, 1858, **47**, 959; Wood, Smith and Jenks, *J.S.C.I.*, 1901, 437.

As only a part of the arsenic is volatilized from coal or coke on combustion, the fitness of a fuel for use in malting depends only on the proportion of "volatile arsenic" present. McGowan and Floris (*loc. cit.*) gave 23 analyses of anthracites for "fixed" and "volatile" arsenic, the average "fixed" arsenic amounted to 0·029 grains As per lb. fuel, the "volatile" arsenic 0·014 grains per lb.

The amount of phosphorus in coals is important if they are to be used for the manufacture of coke for metallurgical purposes. If the phosphorus in the coke is more than 0·02 per cent. it may have a deleterious effect upon the metal produced. In clean British coals 0·05 per cent. is seldom exceeded and in most cases the amount of phosphorus is less than ·005 per cent. Extreme cases of 1 to 2 per cent. have been reported.

Gases in Coal. Coal occludes considerable quantities of gases, principally methane and other saturated hydrocarbons with smaller amounts of oxides of carbon. The occlusion of oxygen and nitrogen has now been disproved by Fischer (see later). The gases are obviously of importance since the evolution of methane (fire damp) in coal mines may lead to dangerous explosions, although the latter are more often due to outbursts of gas from hollows, fissures and porous rock where it has been confined under pressure. Truly occluded gas is not evolved so readily.

The quantity and composition of the gases occluded by coal has been the subject of a great deal of research. The following may be consulted for further details: Porter and Ovitz (U.S. Bureau of Mines Tech. Paper 2, 1911), Darton (U.S. Bureau of Mines, 1915, Bull 72), Monro (*J.S.C.I.*, 1922, **41**, 129 T), Fischer, Peters and Warnecke (*Brenn. Chem.*, 1932, **13**, 209), Lawell and Morris (Amer. I.M.M.E., 1933. See *Colliery Guardian*, 1933, **146**, 1100).

Porter and Ovitz found that with coals of a bituminous and semibituminous nature obtained from "fiery" mines the methane escaped rapidly at first, that its escape ceased in from 3 to 18 months, that during crushing of the sample the evolved methane equalled 25 per cent. of the volume of the coal and that from 50 to 150 per cent. escaped on continued exposure. The maximum evolution was found to be the equivalent of 152 c.c. of methane from 100 gm. coal in 17 months.

Darton (*loc. cit.*) states that gas emitted by coal at the face, or in the laboratory varies in composition, but in most cases contains over 80 per cent. methane. The proportions of the other constituents CO_2, N_2, and O_2 are very variable and appear to be unconnected with the visible appearance of the coal or with the fixed carbon or volatile matter.

Monro has shown that coals may be divided into three classes according to the oxygen/nitrogen ratio of the occluded gases when removed by means of vacuum—

viz. (1) **bituminous coals** . . $O_2/N_2 > 0·264 : 1$ i.e., the air ratio
(2) **lignites** . . . . . . $O_2/N_2 = 0·264 : 1$. These coals have little occluded gas.
(3) **pitch and brown coals** O_2/N_2. Small. —

Monro considers that the gases are present as a solid solution. This, however, does not take into account the pockets of gas which undoubtedly occur in enclosed spaces in the coal seam.

Most of the work which has been carried out on the quantity and composition of the gases occluded by coal has been shown to be of doubtful accuracy by Fischer, Peters and Warnecke (*loc. cit.*). By crushing coal to μ size (0·001 mm.) in a specially constructed gas-tight ball mill from which gases were pumped off continuously, it was found that much greater quantities of gas could be removed and also that the amount removed was independent of the temperature. They also showed by analysis of the nitrogen in these occluded gases that it contained argon to the same extent as the air, and hence proved that the nitrogen and oxygen in the gases is adventitious. Their results are tabulated on a nitrogen-free basis in Table X.

It is to be noted that the composition of the gases obtained is very much the same for coking coal and for anthracite, while the volume of gas obtained from the latter is the remarkable figure of 10 times the volume of the coal itself.

TABLE X

GASES REMOVED FROM COALS GROUND TO μ SIZE IN VACUUM BALL MILL

Coal.	Coking coal from Mathias Stinnes Mine.					Anthracite from Sophia-Jacoba Mine.	
	Banded coal 4 hrs. after mining.	Banded coal stored 1 week.	Banded coal cut from a large piece.	Durain coarse powder < 3 mm.	Vitrain picked pea size.	20–30 mm. particle size.	
Time of grinding, hrs.	1·5	10	4	4·5	3	7 = 5 hrs. at Room temp.	20·5
Temperature . .	Room	Room	100°	Room	Room	2 hrs. at 100°	Room
c.c. gas/100 gm. coal	125	196	130	68	125	880	890
Analysis of Gas :							
CO_2	1·7	2·0	7·4	8·8	5·3	4·2	5·2
CO	1·3	0·5	0·3	0·7	1·0	0·5	0·5
H_2*	[2·5]	[3·0]	[2·5]	[3·7]	[3·6]	[4·0]	[2·7]
CH_4	93·8	93·5	88·6	85·2	89·3	91·1	90·8
C_2H_6	0·7	0·9	0·6	0·8	0·4	0·2	0·8
C_3H_8	0·0	0·1	0·6	0·8	0·4	—	—

* The hydrogen figures are doubtful owing to the method of analysis.

Classification of Coal. The satisfactory classification of coal offers numerous difficulties, and a number of systems have been elaborated. As Curtis (*Chem. and Ind.*, 1932, 350) has stated "no simple classification of coals can be made and an elaborate classification defeats itself." Until something more definite is known of the constituent bodies, resins, humus, etc., it is unlikely that any great advance will be made. It is well known that pure chemical compounds exhibit isomerism, i.e. whilst having the same percentage composition exhibit entirely different properties. Although coal is not a definite compound, the same condition is found. Anderson has pointed out that the splint coals from the Clyde basin are frequently almost identical in composition with the softer coals of the same district, and instances might be multiplied; variations not only in the external physical characters but in the other properties, notably that of caking, are found with coals of practically the same ultimate composition. There is further the gradual change of character from coal of one class to that of another; the agreement in one constituent and disagreement in others, so that hard and fast boundaries are impossible—if they are proposed they are purely arbitrary.

Classification based on such characters as softness, hardness, long flame and short flame, caking or non-caking; or on commercial applications, such as "steam raising," "gas making," etc., are far too general, for it is not uncommon to find a coal described as "steam, gas or manufacturing." On the other hand, classification on the elementary constituents alone of the pure coal substance cannot indicate such important characteristics as fusibility and coking qualities, hardness or friability, gas yielding or burning characters.

When coal is subjected to the action of heat in a vessel under such conditions that, whilst any volatile matter resulting from its decomposition may escape, access of air is prevented, gases and liquid products distil off, and a residue of coke, which includes the ash, remains. The results obtained therefore yield the amount of volatile matter, the coke, and, if the latter is finally heated with access of air, the ash alone remains, so that the loss during this latter operation is due to carbon (usually together with a little hydrogen) which remained in the coke and is termed *fixed* carbon. Such an analysis is termed the *proximate analysis*, and although again it gives no information as to the real compounds existing in the coal, it is invaluable from the information it affords as to the character of the coal and its suitability for practical purposes, besides affording the simplest and probably the best method of classifying the various coals.

A general relationship is found between the results of the proximate examination and the ultimate composition, the volatile constituents being highest when the total carbon is low and the oxygen content high, as occurs with lignites and bituminous coals; whilst with anthracitic coals, where the total carbon is high and the oxygen low, the volatile matter is lower than with any other class of coal.

The general relationship in ultimate and proximate composition of the pure coal substance for typical coals is shown in Table XI.

TABLE XI

ULTIMATE COMPOSITION OF COAL

	Carbon.	Hydrogen.	Oxygen and nitrogen.	Fixed carbon.	Volatile matter.
Lignites and brown coals	69·5	5·5	25·0	52·0	48·0
Splint coal (Fife)	82·0	5·0	12·8	61·0	39·0
Gas coal (Durham)	85·0	5·5	8·2	66·0	34·0
Coking coal	87·3	5·05	6·9	73·5	26·5
Smokeless steam (Welsh)	91·3	4·05	3·9	85·5	14·5
Anthracite (Scottish)	91·1	3·5	4·65	88·5	11·5
Anthracite (Welsh)	91·0	3·9	4·28	93·0	7·0

Broadly speaking, the amount of volatile matter in coal is dependent, then, on the presence of certain bodies rich in oxygen. It does not follow that in two coals of the same ultimate composition the oxygen-containing substances are identical, indeed, as will be shown later, they may probably be of a totally different type, so that it is not surprising that coals identical in ultimate composition behave quite differently under the action of heat, both in the actual yield of volatile constituents and in the character of the coke which results.

For any system of classification it is essential that the coal substance alone shall be considered, variables such as ash and moisture being excluded even although they may be determining factors in the use of the coal. The proximate analysis provides an easy means of differentiating between diverse classes such as anthracites and bituminous coal, but is of little value in sub-dividing such classes. The " ultimate " analysis or the analysis of the elementary constituents is necessary for this and can also be correlated roughly with the proximate analysis.

The different stages or variations in the composition of coals are shown in Table XII which also illustrates the gradual transition from wood, etc. The analyses are typical of the classes but, in making comparisons, it should be remembered that each class merges into its neighbours and coals of intermediate type are common. In the table the gradual elimination of oxygen is seen from 40 per cent. in wood to 2 per cent. in anthracite. At about 18 per cent. oxygen obvious woody structure disappears and at about 10 per cent. the coal begins to possess coking properties. During the removal of oxygen hydrogen is also eliminated partly so that the C : H ratio increases with decreasing oxygen content.

In lignites the ratio is about 13 : 1, in bituminous coals it ranges from 14·5 to 16·4 to 1 and in anthracites is about 27 to 1.

The regular nature of the variations shows where classification systems can readily be attempted. The first attempt was made by Regnault in 1837 and modified later by Grüner in 1874. Regnault classed his coals in terms of their carbon, hydrogen and oxygen contents and in Grüner's modification bituminous coals are divided into five classes as shown in Table XIII.

TABLE XII

Stages in the Transition of Coals

	Wood.	Peat.	Lignite.		Bituminous.				Carbonaceous.	Anthracite.
			Brown.	Black.	1.	2.	3.	4.		
Air-dried.										
Moisture . .	20	20	18	15	10	3	1	1	1	1
Volatile matter, less moisture.	—	50	47	41	35	34	32	30	11	8
Fixed carbon .	—	27	28	32	45	58	62	64	84	88
Ash	0·5	3	7	12	10	5	5	5	4	3
B.Th.U. per lb.	6,400	7,700	9,900	10,200	10,700	13,900	14,300	14,400	15,000	15,000
Ash free dry.										
Carbon . . .	50	60	67	74	77	84	85·6	87	92	94
Hydrogen . .	6·5	6	5·5	5·4	5	5	5	5·3	4	3
Oxygen . .	43	32	26	19	16	8	5·4	4·7	2	2
Sulphur and nitrogen . .	0·5	2	1·5	1·6	2	3	4	3	2	1
B.Th.U. per lb.	8,000	10,000	13,200	13,900	13,400	15,100	15,200	15,300	15,800	15,600

Bituminous	1.	Lignitious, long-flame steam and house coal.
,,	2.	Para-bituminous, hard steam, house and manufacturing coal.
,,	3.	Para-bituminous, gas and coking coal.
,,	4.	Ortho-bituminous, coking coal (Durham).

TABLE XIII

Regnault–Grüner Classification of Bituminous Coals

No. of class.	Character of coal.	Carbon.	Hydrogen.	Oxygen.	Ratio $\frac{O}{H}$	Volatile matter.	Nature of coke.
I.	Dry, long flame, non-caking	75–80	4·5–5·5	15–19·5	4–3	40–50	Powdery or slightly coherent.
II.	Fat, long flame	80–85	5·0–5·8	10–14·2	3–2	32–40	Caked, but friable.
III.	Fat, properly so called	84–89	5·0–5·5	5·5–11·0	2–1	26–32	Caked, moderately compact.
IV.	Fat, short flame	88–91	4·5–5·5	4·5–6·5	1	18–26	Caked, very compact, lustrous.
V.	Lean coals —anthracite	90–93	4·0–4·5	3–5·5	1	10–18	Powdery or slightly coherent.

The range of composition for a class is not wholly consistent with that of this class as found in Great Britain, so slight adjustment is required. Further, the important "Navigation" and "Smokeless Steam Coals," very distinct classes, require inclusion. In the coals of low rank, although lignite proper only occurs in very small quantity in Great Britain, there are "dry" coals, with high oxygen content, between the lignites and the usual steam "non-caking long flame coals," which seem to demand special groupings, and for these the terms lignitious and ligno-bituminous have been adopted. Brame's modified and extended form of Grüner's Classification is given in Table XIV.

TABLE XIV

Grüner Classification modified for Coals of Great Britain

No. of class.		Name of class.	Carbon.	Hydrogen.	Oxygen.	Volatile matter.
I.		Lignitious	75–80	4·8–5·5	12–20	35–47
II.		Ligno-bituminous	78–84	4·5–6	8–13·5	35–45
III.	Bituminous	Long flame, non-caking (steam, etc.)	82–86	5–6	6–12	30–40
IV.		Long flame, partly caking (gas)	82–86	4·5–5·5	5–9	30–40
V.		Short flame (coking)	85–89	4·5–5·5	4–7·5	20–30
VI.		Semi-bituminous	89–92	4–5	2–4·5	13–20
VII.		Semi-anthracite	91–93	3–4·5	3–5	8–13
VIII.		Anthracite	over 92·5	below 4	below 3	below 8

A closely allied classification on the basis of the Grüner system has been adopted by W. A. Bone, the main groupings being lignites, bituminous, semi-bituminous and anthracites, with sub-division of the bituminous into non-caking long flame, caking long flame, hard coking and hard coking short flame, and the anthracite group into anthracitic and anthracite.

It must again be emphasized that no such system can be rigid; for example, a gas coal towards the lower limit of volatile matter may be satisfactorily worked for coke in a suitable oven, and a semi-bituminous caking coal may be equally good for coking whilst not so well suited for burning owing to its caking properties.

A number of other classifications have been attempted since. The most important of these are described below.

1. Frazer (Pa. 2nd Geol. Survey, Rept. M.M. 879).

In this scheme the ratio of fixed carbon to volatile matter was used. The system failed mainly because of considerable overlapping of classes and limitation to one particular coalfield.

TABLE XVI

SEYLER'S CLASSIFICATION OF COAL

Carbon.	Anthracitic.	Carbonaceous.	Bituminous.			Lignitous.	
			Meta-	Ortho-	Para-	Meta-	Ortho-
	Carbon over 93·3 per cent.	93·3–91·2.	91·2–89·0.	89·0–87·0.	87·0–84·0.	84–85.	80–75.
Per-bituminous genus. Hydrogen > 5·8 per cent.	—	—	Per-bituminous (per-meta-bituminous)	Per-bituminous (per-ortho-bituminous)	Per-bituminous (per-para-bituminous)	Per lignitous	
Bituminous Genus Hydrogen 5·0–5·8 per cent.	—	Pseudo-bituminous species	Meta-bituminous	Ortho-bituminous	Para-bituminous	Lignitous Meta	Ortho
Semi-bituminous Genus Hydrogen 4·5–5·0 per cent.	—	Semi-bituminous species (ortho-semi-bituminous)	Sub-bituminous (sub-meta bituminous)	Sub-bituminous (sub-ortho-bituminous)	Sub-bituminous	Sub-lignitous Meta	Ortho
Carbonaceous Genus Hydrogen 4·0–4·5 per cent.	Semi-anthracitic species	Carbonaceous species (ortho-carbonaceous)	Pseudo-carbonaceous (sub-meta-bituminous)	Pseudo-carbonaceous (sub-ortho-bituminous)	Pseudo-carbonaceous (sub-para-bituminous)		
Anthracitic Genus Hydrogen < 4 per cent.	Ortho-anthracite	Pseudo-anthracite (sub-carbonaceous)	Pseudo-anthracite (sub-meta-bituminous)	Pseudo-anthracite (sub-ortho-bituminous)	Pseudo-anthracite (sub-para-bituminous)		

geographical one, the hydrogen lines corresponding to parallels of latitude and the carbon lines to those of longitude ; just as the position of a place is defined geographically by defining latitude and longitude so the position of a coal can be defined by quoting its C : H values. Then, by reference to a chart the nature of the coal is at once clear. Such a system of definition should be clearer than a system of names.

Later Seyler added to his chart other values in the form of isovalent lines showing the regular variation of different properties of coals.

In the chart the common types of coal fall within the rectangular areas to the left and together form a curved band which is sometimes termed the coal band and resembles that of Parr. Coals of higher hydrogen content (perhydrous) are bogheads and cannels of less common occurrence. Subhydrous coals are fusain and certain durains.

The isovalent lines are as follows. The lines of equal calorific value (isocals) slope upwards from left to right while those of equal volatile matter (isovols) cross these at right angles. The former are parallel, equally spaced lines, following Dulong's law, but the latter are less regular outside the region of 10 to 40 per cent. volatile matter. In themselves these lines have no great significance, but their insertions indicate means of correlating calorific value and volatile matter. The isocals are also lines of equal air requirements for the combustion of the coal and have been correlated by Seyler (*loc. cit.*) and Rosin and Fehling (*Das It. Diagramm*, Berlin, 1929), with flue gas volumes, calorific intensity and flame temperature under conditions of adiabatic combustion. In the chart (Figure 4), Seyler has added a number of scales showing the combustion characteristics appropriate to the isocal lines. The top and bottom scales are metric and British units respectively.

For a fuller account of Seyler's diagram reference should be made to the original papers, particularly the following—*Proc. of S. Wales Inst. of Engs.*, 1931, **47**, No. 3, Part II ; *J.S.C.I.*, 1933, **52**, 304T ; *J. Inst. of Fuel*, 1934, **7**, 181.

The chart can be shown in a much more simple form showing the C : H axes and the coal band only. A simplified chart has been prepared by King (*Prep. Selection and Dist. of Coal*, Colliery Guard, Ltd., 1931). Figure 4.

That there is a discontinuity in the coal band has been shown by E. S. Grumell (*Trans. Inst. Min. Eng.*, 1931, **81**(**2**), 214 : **81**(**3**), 308). When the calorific value of a large series of coals is plotted against their carbon content a coal band is obtained which shows a sharp bend at about 86 per cent. C. indicating that above this point the coals diverge from the Dulong formula. Below the point agreement of observed calorific value with that calculated from the Dulong formula is found within reasonable limits. Grumell prefers to consider dull and bright coals separately as having different sources and shows that their coal bands do not coincide. A coal band of this type is a useful guide to fuel composition since it is comparatively narrow in both dimensions below the band at 86 per cent carbon. For example with bright coals the iso-calorific lines may contain coal differing by 1·2 per cent. of carbon and the iso-carbon lines coal differing by only 155 calories. It seems probable that even these margins may be reduced by more accurate analysis.

COAL CLASSIFICATION AFTER SEYLER

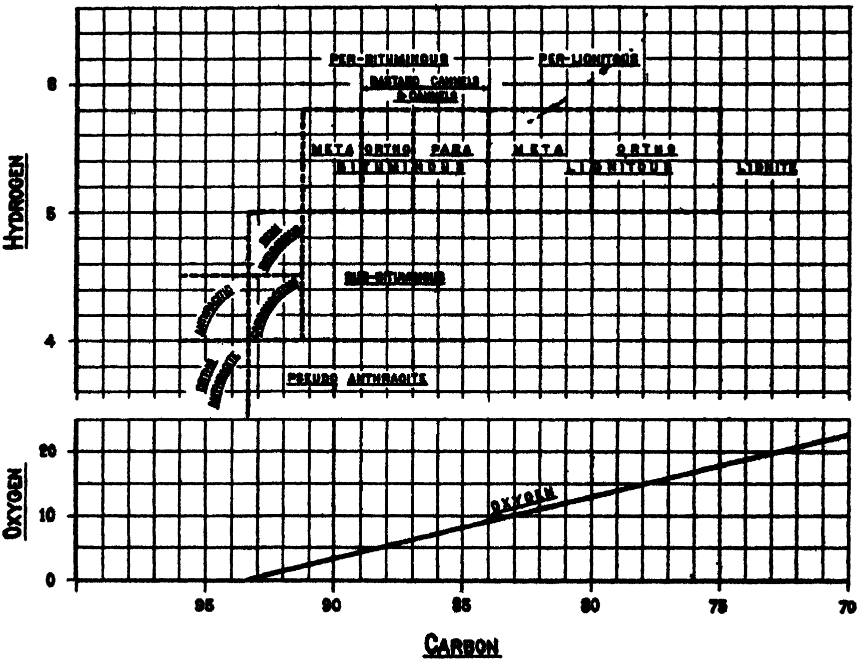

FIG. 4.

CHAPTER V

COMMERCIAL AND EMPIRE COAL

LIGNITE

Nature and Occurrence of Lignite. Reference has been made already to the intermediate position which lignites occupy naturally between peat and coal. Lignites vary very widely in character and composition according to the metamorphosis which the lignin of the plant has undergone, from bituminous wood to material so closely resembling " dry " bituminous coal that it is difficult, if not impossible, to distinguish between them. They are characteristic of strata more recent than that of the true coal formations, but frequently have become so altered by local conditions as to merge into bituminous coals or even semi-coked material resembling anthracite.

Lignites are of later (Tertiary) geological formation than coal. In Great Britain there are only limited deposits, the brown lignite of Bovey Tracy, Devonshire, but in Europe, North America, Australia, New Zealand and India the deposits are extensive, brown lignites being sometimes found in seams 100 ft. thick so near the earth's surface that they can be quarried at very low cost.

Lignites occur in a number of well-defined forms and can be classified by their physical characteristics :

(1) Woody or fibrous brown coal having the structure of wood.

(2) Earthy brown lignite, compact but friable.

(3) Brown coal, having a slight woody structure, a slaty cleavage and a dark-brown colour.

(4) Bituminous lignite or "pitch-coal," black in colour with a conchoidal fracture. It resembles coal and sometimes anthracite in appearance. This form has been classified by the U.S. Geological Survey as " sub-bituminous " coal.

As mined, brown lignites usually contain a very high percentage of moisture, much of which is retained on air-drying ; Bischoff records an average of 44 per cent. on German lignite ; Schrötter 57 per cent. on Austrian samples.

Black lignites contain less moisture, normally 14 to 16 per cent.

Composition of Lignite. So many carbonaceous fuels of distinctly vegetable character are classed as lignites, frequently on their geological occurrence, that it is difficult to state an approximate composition.

Some idea of the relative occurrence of these in Europe is obtainable from the following analyses of 62 samples:

TABLE XVII

COMPOSITION OF LIGNITES (European). (Calculated to the dry, ash-free fuel)

Range of Carbon.	No. of samples.	Carbon per cent.		Hydrogen per cent.		Oxygen per cent.	
Below 60 per cent. .	5	**57·1**	59·2 55·1	**5·8**	6·1 5·1	**37·1**	38·9 34·8
60–65 per cent. . .	8	**63·3**	64·8 62·0	**5·6**	6·6 4·7	**31·1**	32·5 29·2
65–70 " . .	25	**67·1**	70·0 65·2	**5·5**	6·7 4·8	**27·4**	29·7 25·0
70–75 " . .	19	**72·6**	75·0 70·6	**5·8**	7·4 4·6	**21·6**	24·0 18·2
75–80 " . .	2	**76·3**	76·6 76·0	**7·3**	8·3 6·3	**16·4**	17·7 15·1
Above 80 " . .	3	**84·4**	86·6 82·2	**5·4**	6·6 3·9	**10·2**	13·2 9·0

NOTE.—In all tables where the composition of solid fuels is given as above, the mean figures are shown in larger type, and the maximum and minimum figures in small type.

It will be seen that over 90 per cent. of the samples in Table XVII contain under 75 per cent. of carbon and over 20 per cent. of oxygen. The last three have a composition in good agreement with a large number of English coals (for which the term "lignitous" has been accepted. Since classification based on geological evidence is thus capable of including totally dissimilar fuels, it is agreed that lignites proper contain under 75 per cent. of carbon and over 20 per cent. of oxygen.

The volatile matter in lignites falling within the above range is seldom less than 48 per cent.; it usually exceeds 50 per cent., but in a large number of cases the ratio of volatile matter to fixed carbon is approximately 1 to 1.

The following analyses are typical of the most important lignite deposits:

TABLE XVIII

ANALYSES (DRY, ASH-FREE) OF LIGNITES

	Carbon.	Hydrogen.	Sulphur.	Nitrogen.	Oxygen.	B.Th.U. per lb.
Brown:						
Heathfield, Devon . .	65·7	5·5	2·1	1·0	25·7	11,200
Germany	69·0	4·9	0·9	0·7	24·5	11,300
Australia (Morwell) . .	64·9	4·8	0·8		29·5	10,300
Black:						
Saskatchewan, Canada .	73·0	5·9	0·8	1·5	18·8	13,050
New Zealand	73·0	5·4	0·5	1·1	20·0	12,620
Burma	70·5	4·5	1·0	1·0	23·0	11,200

Calorific Value of Lignite. This will be dependent to a very large extent upon the closeness or remoteness of its composition in relation to wood on the one hand and lignitous coals on the other, and to the amount of moisture and ash present.

The calorific value of the combustible may range from 5000 to 7500 calories (9000 B.Th.U. to 13,500 B.Th.U.). In practice the high moisture content is a serious disability in that it greatly reduces the net heat units available.

Lignite as Fuel. The high percentage of moisture and sometimes of ash generally present makes lignite an inferior fuel to coal. Brown coals are generally air-dried to 12–15 per cent. of moisture and briquetted. These briquettes, apart from a tendency to spontaneous combustion, form an excellent fuel, having a calorific value of 9000 B.Th.U. at 15 per cent. moisture. The black lignites " weather " badly on exposure to air and disintegrate rapidly to slacks. For this reason attempts have been made to produce from them a lump fuel by carbonization and subsequent briquetting of the coke, but as yet without complete success. In some places (New Zealand) black lignites are mixed with coking coals and used for gas manufacture. The reason is, however, mainly in order to control the inordinate fusibility of the caking coal.

Yields obtained by the carbonization of Saskatchewan lignite are quoted by Stansfield :

Moisture content 31·8 per cent. : Gas, 3505 cu. ft. (c.v. 385 B.Th.U. per cu. ft.) ; tar, 5·9 gals. ; ammonium sulphate, 11·4 lb. ; carbonized fuel, 1020 lb. per ton.

In Germany large quantities of brown coal are carbonized, yielding from 17 to 26 per cent. by weight of tar per ton of *dry* material. Large quantities of the tar have been treated by catalytic hydrogenation at high pressures, and it has been stated that from this source 100,000 tons of motor spirit have been obtained per annum.

Lignite coke is specially liable to spontaneous ignition. It has served as a source of " activated " carbon.

Lignite has been employed successfully in gas producers. Tests made in the United States (U.S. Geol. Survey, Bull. 416, 1910) have indicated consumption 2 lb. of lignite at 26·6 per cent. moisture per B.H.P. developed.

CANNEL COAL

This variety of coal differs in character from the lignites and true bituminous coals, and the organic matter from which it was derived differed no doubt from that from which the other varieties were produced. According to Bertrand and Renault, Boghead cannels are composed mainly of gelatinous algæ ; but Jeffrey disputes this, and contends that they are composed mainly of the spores of vascular cryptograms. Recent work upon the examination of micro-sections of various cannels tends to confirm the former opinion. Fish and other animal remains are found frequently with cannel coals, which, together with the usual form of deposition in beds thinning out at the edges, indicates that they were deposited from fairly stagnant water.

Cannel coal has been of great importance in the manufacture of gas, since on distillation it gives a good gas yield of exceptionally high candle power. When illuminating value became of less importance, owing to the extensive use of the incandescent mantle, and later, by the introduction of calorific value as a basis of supply instead of candle-power, the use of cannel in the manufacture of coal gas greatly declined. Cannel derives its name from the candle-like flames emitted on burning; some varieties split with a crackling noise on heating, and are termed “ parrot ” coals; others, from the odour emitted on burning, as “horn ” coal.

The Torbane Hill or Boghead cannel coal, found only in the Armadale district of Scotland, was a very rich species of cannel yielding as much as 120 gallons of oil per ton. This material is now mainly of historic interest since the field was exhausted in 1862. It was characterized by a high percentage of hydrogen and of volatile matter and a very high ash.

The proximate and ultimate constituents of cannel or Boghead coals vary within such wide limits that it is impossible to correlate properties and composition, but clearly it must be due to the gelatinous algæ that cannels on distillation give a much higher proportion of stable gaseous hydrocarbons than bituminous coals.

TABLE XIX

Composition of Boghead and Cannel Coals

	Total carbon.	Hydrogen.	Oxygen.	Fixed carbon.	Volatile matter.	Ash on dry coal.
Boghead cannel (Torbane Hill) . . .	78·1	10·43	11·47	12·2	87·8	33·0
St. Helens . . .	79·0	6·05	14·97	47·25	52·75	3·05
Wigan	82·4	5·70	11·90	—	—	2·70

The proportion of volatile matter to the fixed carbon usually is high (50–50), but there are many exceptions in which this ratio is no higher than in an ordinary bituminous coal (33–66). In Lesmahagow cannel, a former gas-making standard, the volatile matter is given as 54 to 56 per cent. and the fixed carbon as 44 to 46 per cent. of the pure coal.

On distillation cannel coal yields tar of a more paraffinoid character than bituminous coal. The yields also are much higher, as much as

90 gallons per ton (dry, ash free). The Fuel Research Board have shown that 54 gallons are obtainable from Welbeck cannel (Rep. of Test on Fusion Retort, 1926).

BITUMINOUS COAL

As stated above, the black lignites merge into a class of lignitous coals. These in turn merge into the bituminous coal species without any clearly defined division. The lignitous coals and the bituminous coals are normally regarded as one class of widely divergent properties which vary gradually and regularly from one end of the class to the other. The bituminous species comprise coals containing from 24 to 40 per cent. of volatile matter and 84 to 91·2 per cent. of carbon. Lignitous or non-caking bituminous coals contain over 10 per cent. of oxygen, while the high-rank coking coals at the other end of the scale contain less than 5 per cent. As devolatilization of the coal increases, the ability of bituminous coal to form a hard coherent coke when carbonized also increases.

In the seam, all bituminous coals exhibit a banded structure, the coal showing alternate bands of bright and dull coal arranged parallel to the bedding plane. Four types of band have been defined in this country by Stopes as vitrain, clarain, durain and fusain and two bands have been defined in American coals by Thiessen as attritus and anthraxylon. The anthraxylon corresponds to the vitrain and clarain, and the attritus to the durain.

Vitrain has a glassy lustre and normally occurs in very thin bands about 0·2 inch thick. In thin sections it is pale brown and translucent and microscopically appears almost devoid of structure. Clarain appears in thicker bands and is less bright and less brittle than the vitrain. It is translucent in thin sections and shows disintegrated plant remains when examined under the microscope. Durain is the dull hard coal which occurs in definite bands from a fraction of an inch to sometimes a large proportion of the seam. It is hard and strong. Microscopically it contains plant remains embedded in a granular matrix which is opaque in thin sections. Fusain occurs chiefly in lenticles and forms points of weakness in banded coal. It is dull, granular and fibrous and usually very friable. Microscopically it consists of woody tissue, opaque in thin sections.

Photomicrographs of typical sections are shown in Plate I, and other data on p. 42.

The measurement and examination of the bands in bituminous coal seams form a means of exploring the variations which occur in the different parts of the coalfield.

It has been shown that the amount of volatile matter present in the coal substance is an important property of coal and affords a useful basis of classification. The volatile matter governs largely the character of the combustion, determines the suitability of a coal for special purposes, and the design of grates and furnaces for the most efficient combustion of the different classes of coal.

Flame is produced largely by the combustion of these distillation products, which form a mixture of hydrocarbon gases, tarry vapours, etc. Smoke results entirely from their incomplete combustion. It follows that the proportion of the total heating units of a coal derived from combustion on the grate and in the combustion spaces respectively varies with the amount of volatile matter. Schniewind estimates that in a coking coal 72 per cent. of the heat units are available in the coke, 23 per cent. in the gases, and 5 per cent. in the tar. For bituminous coals it may be taken approximately that one-third of the heat units are present in the volatile matter. Owing, however, to variation in composition of the volatile matter, its heating value is not always proportional to the amount in different coals.

Where intense local heating is required, it follows that a fuel with little volatile matter must be employed, such as anthracite; whereas, on the other hand, where long flame is essential, as in a reverberatory furnace, the proportion of volatile matter, which provides the necessary combustible gases, must be high; that is, the greatest number of heat units possible must be obtained away from the grate.

For steam-raising these considerations obviously will govern the relationship between grate area and combustion space, the admission of air above and below the grate, for the best results to be obtained for coal of a given type. For steam-raising then, although high calorific value is essential, other considerations are equally important, and these depend largely on the amount of volatile constituents. The effect of ash and moisture has already been dealt with. The ignition point of coals low in volatile matter is high (p. 6), and generally the rate of combustion is low, so that strong draught is necessary; bituminous non-coking coal ignites easily, and burns readily with moderate draught.

Constam and Schläpfer have investigated the influence of volatile constituents on combustion (see *Eng.*, 1909, **90**., 93), and found that coals containing about 20 per cent. (calculated on the combustible) yield the highest temperature and thermal efficiency. With too high volatile matter gases escape unburnt, and too much excess air must be admitted above the grate; and, on the other hand, with low volatile matter an excessive air supply is requisite for the fuel on the grate. Further, whilst the carbon from any coal yields the same number of heat units, equal weights of the volatile constituents develop comparatively less heat as the volatile matter increases. The highest economic efficiency will be attained, therefore, with coals of medium volatile content, say, from 16 to 23 per cent.

The steaming capacity, or output of the boiler, will be dependent on the furnace temperature, which again is dependent on calorific value, but more especially on the rate at which the coal can be consumed, anything tending to lower this being prejudicial. The influence of ash has been considered; very small coal, by interfering with the free passage of air, will greatly affect this, so also will tendency to cake, which, if the draught is moderate, may seriously lower the rate. It follows, therefore, that the ratio of grate area to heating surface and the draught conditions for a given coal may yield far from the best result with another coal, and therefore that the selection of a coal for given conditions is dependent on many considerations outside of calorific value. Although fine coal interferes with combustion, small coal frequently is an excellent fuel if free from dust; uniformity of size is desirable in general.

By far the largest proportion of coal in common use for steam-raising contains very much higher volatile matter than that found most economical by Constam and Schläpfer. Complete combustion without objectionable smoke is difficult to ensure, even with considerable excess of air, unless some suitable form of mechanical stoker is employed. Good efficiency can be obtained, but this necessitates careful and scientific control of the combustion by attention to the composition of the flue gas; without such attention the losses generally are enormous.

In producer-gas practice the volatile constituents of the fuel govern entirely its suitability for different types of producers, or, conversely, the design of the plant for the most economical fuel available. Again, the presence or absence of volatile constituents will determine largely the character of the gas; where present the latter will obviously consist of a mixture of the products of destructive distillation (coal gas) with producer gas proper, and since the former has the higher calorific value, the mixture should be richer than that obtained from a fuel yielding practically only producer gas, such as from anthracite. Part of the products of destructive distillation of a bituminous fuel must be tar, and it is the difficulty of removing this in most suction plants that limits the choice of fuel to anthracite or coke. The question of tar is not necessarily one of quantity, since the tar from certain forms of coal can be dealt with more easily.

Caking coal is admissible only in special types of producer. In the normal type it would need constant poking to work it, and large channels would form, through which the blast would pass and fail to yield good combustible gas. Uniformity of size is another important factor. The influence of the fusibility of the ash has been dealt with already (p. 55), but it should be mentioned again that fusibility is often more important than amount.

Coking coal is distinguished from other bituminous coals by its property of undergoing a partial fusion when subjected to heat, and, decomposition ensuing at the same time, the gases evolved give a cellular structure to the coke. The coal loses its original form and structure entirely, thus distinguishing it from coals which do not possess this property of fusion, the cokes from the latter retaining more or less the original shape of the pieces of coal. Necessarily there are intermediate grades between these extremes, and a coal may possess the fusion property only in a moderate degree, so that selection of a suitable form of oven and carbonizing conditions is essential to the production of serviceable coke from it.

Reference has been made already to the difficulty of correlating this fusing property with the ultimate composition of the coal. Results from a particular coalfield are sometimes fairly concordant, and this has given rise to the fixing of dogmatic limits of composition within which coking properties are found, but these same limits are frequently quite inapplicable to another coalfield. It is certain, however, that as the coals approach the lignites on the one hand, and anthracites on the other, no tendency to coke is observed.

Authorities are agreed that the only sure guide to determine whether a coal is suitable for coking is a practical test. Valuable information often is to be gained from the nature of the coke obtained during proximate analysis in a platinum crucible, but the rate of heating in some cases may modify considerably the result. Rapid heating will, with some coals, drive off all the volatile hydrocarbons so quickly that the cementing action of the pitch has little chance, whereas slow heating may yield a fair coke. It is therefore difficult to relate the results from the crucible test to practice, where the rate of heating is so much slower.

The Gray-King assay is typical of a number of carbonization assay methods for the evaluation of coals for this purpose. The method (p. 349) gives the character of the coke and yields of products at 600° C. or at 900° C. Lessing (p. 349) has proposed a similar method.

In coking practice the accepted method of test of small samples is the " box " test in which a box containing about 300 lb. of the test coal is placed on the bottom of an oven before charging. The box is recovered later and the coke examined.

The Campredon coking test is designed to give a " caking index " for various coals; it represents the amount of sharp sand which 1 gram of the coal is capable of just binding into a coherent mass. A good coking blend will cohere with 14 to 16 grams of sand. The sand method has been standardized and issued as an accepted method by the Fuel Research Board. The " caking index " is the ratio of the weight of graded sand to the weight of coal which under the standard conditions of carrying out the test (detailed on p. 349) give a coke capable of supporting without crushing a 500-gramme weight, at the same time not yielding more than 5 per cent. of non-coherent powder on the weight of mixture. Good coking coals give "caking index" figures of 16 or over.

Objection has been taken to the use of sand, since in some cases it is not inert to the coal ash. Electrode carbon, suggested by Sinnatt and Grounds (*J.S.C.I.*, 1920, **39**, 83 T.), is a good alternative.

NAVIGATION, BUNKER AND SMOKELESS STEAM COALS

No term descriptive of coal is employed so widely as "steam coal" and includes all coals other than strongly-coking coals and anthracites. Any of the bituminous steam coals already described can be used for navigation and bunker purposes, but the most valuable are the semi-bituminous or carbonaceous coals. These coals represent the transition stage between bituminous coking coals and anthracite and occur chiefly in South Wales although similar seams occur in East Kent. Those containing about 5 per cent. of hydrogen and 20 per cent. of volatile matter are caking steam coals; those containing up to 4·7 per cent. hydrogen and 18 per cent. volatile matter are second-class Admiralty steam coals; those containing 4·0 to 4·5 per cent. of hydrogen and 10–15 per cent. of volatile matter form the celebrated Welsh steam or first-class Admiralty steam coals.

Coal of this latter type is particularly valuable in having a low ash content and a high calorific value (15,800 B.Th.U. per lb. on the dry, ash-free fuel) and for its smokelessness and free-burning qualities on the boiler grate.

ANTHRACITE

Anthracite is the least widely distributed of the coals and one of the most valuable. The most notable deposits are those of South Wales and Pennsylvania, in both of which anthracite of very high quality is obtained. Anthracite is hard and lustrous, and does not soil the fingers. The ash is lower than in bituminous coals. Owing to its low content of volatile matter it burns almost without smoke and does not soften or cake. This, with its high density, makes it a particularly valuable fuel for use in stoves.

In many parts coals of similar composition to anthracite are found, which have resulted from the intrusion of igneous rocks into bituminous coal measures. Here the ash is higher than in the unaltered coal, and such coal may be regarded almost as a semi-coke. True anthracite appears to derive its special characteristics from the nature of the original deposited carbonaceous matter, or from changes brought about in it very shortly after deposition, and existed as anthracite before denudation or serious disturbance of the strata took place. Where great subsequent disturbance of the strata has taken place, the anthracite still has the same characters and composition, but has become broken down into a coarse powder called "culm."

Anthracites proper contain less than 8 per cent. of volatile matter with 93 per cent. or over of carbon. Pseudo-anthracites, e.g. the Scotch anthracites, are higher in volatile matter and approximate to about 12 per cent.

The chief industrial uses of anthracite are steam-raising, central-heating and malt and hop drying.

Comparative Analyses

Comparative analyses of typical coals are shown in Table XII (p. 63), analyses of wood and peat being included to show the general trend of changes in composition.

COMPOSITION OF COALS OF THE BRITISH EMPIRE

Great Britain. There are 40 detached areas in Britain in which coal-bearing strata occur. All of these form part of four main tracts in which the original plant debris was deposited: (i) Central Scotland, (ii) Northumberland, Durham and Cumberland, (iii) North Wales, Lancashire, Yorkshire and Midlands, (iv) South Wales, Forest of Dean, Bristol and Somerset. Geological information regarding the fields is fairly complete (see Walcot Gibson, *Coal in Great Britain*, E. Arnold and Co., London), but until recently reliable data as regards the analyses of British coals was difficult to find. Since 1922, however, the Fuel Research Division of the Department of Scientific and Industrial Research has started "survey" work upon the most important seams. Nine local laboratories have been set up in the coalfields and are conducting investigations of the principal seams in each. Arrangements have been made to cover 96 per cent. of the coal-bearing areas. In addition to the examination of seams the surveys include the analysis of samples of commercial grades, i.e. the fractions into which the coals are divided for sale by considerations of size and quality. Eventually the series of reports should form a reliable guide to British coals; the reports are available at H.M. Stationery Office.

Detailed information of a more general character is available in *Mineral Resources*, published by the Imperial Institute in 1920 and in *Resources of the British Empire: Fuel*, by G. W. Andrew (E. Benn, London, 1924).

Space permits only of a brief description of the types of coal found in the different coalfields.

The Scottish coals are in general bituminous, high in volatile matter and of low coking power. Coking coals are found mainly in the Lanarkshire field. but these are not of high quality. A survey of the coking coals of Scotland was made by Gray in 1917 (Fuel Research Survey Paper No. 15). In many areas the coal seams are interbanded with cannel. In the Lanarkshire and Fifeshire fields there occur pseudo-anthracites formed by igneous intrusion.

The Northumberland and Durham field is divided by the Tyne into two distinct parts. North of the Tyne the coals are practically non-coking and are high in oxygen content; they are, therefore, steam and producer coals. South of the Tyne the seams develop coking properties and south and west of Durham they provide the best coking coal in the country. Certain of the main seams of the field vary considerably in properties from place to place.

The Cumberland field is small; the coals being mainly coking and gas coals.

The Lancashire field contains a number of seams of excellent coking and gas coals. Much of these are sold for general and household purposes. The North Wales field contains somewhat similar coals, but of lower coking power.

The Yorkshire, Nottingham and Durham field is our largest coalfield, yielding about 80 million tons of coal per annum. The coal seams are all bituminous, but vary widely in properties. Coking properties tend to decrease in a southward direction with a corresponding increase of oxygen content and decrease of carbon content.

The North Staffordshire field is very much faulted and the properties of the coal in the seams therefore vary very widely. The upper seams are coking and the lower vary from coking in the west to non-coking in the east. In South Staffordshire, Leicester and Warwick, the coals are of the same weakly coking type.

In South Wales the coal shows a gradual transition from bituminous coking and gas coals in the east and south-east to semi-anthracitic coals and anthracites in the west and north-west. The coking coals of the east are continued in the small Forest of Dean area and in the Bristol and Somerset fields where they are of higher coking power and higher volatile matter.

In East Kent the coal seams are deep; the coal is of low volatile matter varying from 10 to 22 per cent., those seams containing 18 to 22 per cent. having a very high coking power, those of low volatile matter resemble the carbonaceous coals of South Wales. The Kent coals are characterized by high friability.

The following tabulation (Table XXI) gives analyses quoted from the Fuel Research Survey Reports and, where these are not yet available, of data obtained from other reliable sources. It should be realized that one analysis cannot represent all the coal in a seam since that seam will vary throughout the area. In addition seams are seldom sold as such. Coal for sale is more frequently either a portion of the seam, e.g. "hards" or "softs" or a "size-fraction" which may include the same "size-fraction" from one or more other seams.

The Survey Reports, in addition to analyses, contain Gray-King carbonization assays, ash-fusion temperatures and other relevant data. The seams covered so far include the following:

Lancashire.—Arley, Ravine, Smith, King, Wigan Four-Foot and Lower Mountain Mine seams.

Yorkshire.—Correlation of Yorkshire, Notts and Derby Fields; Parkgate, Barnsley and Silkstone seams; South Yorkshire commercial grades.

Northumberland and Durham.—Yard, Main Brockwell and Hutton seams.

North Staffordshire.—Coalfields.

Scotland.—Scottish Coking and Furnace coals, Kinneil coal.

Somerset.—Parkfield coal.

Australia. Large deposits of coal are found in New South Wales, Queensland, and there are smaller fields in South Australia, Victoria, West Australia and Tasmania.

In New South Wales the coalfield covers over 8000 square miles, the coal measures containing over 70 ft. of workable coal in 10 or 12 seams. Louis gives the following proximate analyses for three seams:

	Moisture.	Ash.	Volatile matter.	Sulphur.
Bulli (Sydney)	1·0	10·7	23·1	0·5
Lithgow (West)	1·8	12·1	31·4	0·7
Borehole (North)	2·0	8·7	36·0	0·5

The first two are coking coals, and the third a house and gas coal. The coals of the middle measures are more friable and that of the lower measures is hard and suitable for domestic purposes and steam-raising.

New South Wales also contains seams of shaley coal of Triassic age and some lignite.

In Queensland the coal is very variable owing to faulting, varying from anthracitic to gas coal. Lignite is found in seams of 57 ft.

In Victoria there is little true coal but immense deposits of lignite. Louis gives the analysis of Wonthaggi (house) coal as ash 9·2, moisture 6·9, volatile matter 28·3. The lignite deposits at Morwell have been described by Bone (*Proc. Royal Soc.*, 1921, 99 A, 236) and comprise seven beds totalling over 1000 ft. On mining the lignite (brown coal) is high in moisture, 40 to 60 per cent., but loses half of this in air-drying.

TABLE XX

ANALYSES OF BRITISH COAL SEAMS (percentages of the dry ash-free coal)

	Carbon.	Hydrogen.	Nitrogen.	Sulphur.	Oxygen and errors.	Volatile matter less moisture.	Calorific value B.Th.U. per lb.	Type.	Reference.
Scotland :									
Lanarkshire : Main and Ell	80·1	5·3	1·3	1·6	11·7	36·5	14,520	Household, slightly coking.	Report F.R.B. 1920–1.
,, Virgin (Uddingston)	81·4	5·4	2·1	0·8	10·3	41·5	14,600	Household and gas, medium coking.	Rep. on Maclaurin Plant. 1929, D.F.R.
Linlithgow : Six Foot (Kinneil)	84·1	5·2	1·6	0·4	8·7	36·9	14,920	Gas or steam, slightly coking.	Survey Paper No. 11.
Clackmannan : Hawkhill (Tullygarth)	80·9	5·5	1·8	0·9	10·9	43·5	14,270	Household, non-coking.	Rep. on Crozier Plant. 1927, D.F.R.
Northumberland :									
Yard (Ashington) . . .	83·1	5·3	2·0	0·9	8·7	37·7	14,570	Household.	Survey Paper No. 21.
Main (Seaton)	80·8	5·5	1·7	1·2	10·8	40·6	14,580	Bunker, steam.	,, ,, No. 22.
Beaumont	84·6	5·4	1·7	1·5	6·8	37·1	15,200	Household.	Grumell.*
Durham :									
Brockwell (Nr. Durham) .	87·4	5·2	1·7	0·8	4·9	28·3	15,480	Coking.	Survey Paper No. 24.
Hutton (Nr. Chester-le-Street)	87·0	5·3	1·6	1·1	5·0	32·6	15,510	Gas.	,, ,, No. 27.
Busty	87·8	5·3	1·4	0·9	4·6	29·4	15,660	Coking.	Grumell.
Cumberland :									
Main	84·8	5·4	1·5	1·0	6·3	33·0	15,250	Coking.	*Prep., Sel. and Dist. of Coal.*
Lancashire :									
Arley (Atherton) . . .	83·8	5·1	1·4	2·0	7·7	37·6	15,040	Coking, gas.	Survey Paper No. 3.
Ravine (Bickershaw) . .	83·4	5·3	1·6	3·5	6·2	38·8	15,170	Coking, gas.	,, ,, No. 4.
Smith (Atherton) . . .	83·3	5·3	1·7	1·7	8·0	39·9	15,090	Coking, gas.	,, ,, No. 5.
King (Burnley)	82·9	5·2	1·6	3·5	6·8	36·2	15,190	Manufacturing, medium coking.	,, ,, No. 6.
Wigan, Four Foot (Garswood)	82·4	4·9	1·8	2·0	8·9	40·2	14,720	Coking, gas.	,, ,, No. 10.
Lower Mountain Mine (Altham)	85·4	4·9	2·1	0·7	6·9	32·0	15,020	Coking.	,, ,, No. 19.
North Wales :									
Main	82·9	5·2	1·6	1·1	9·2	38·0	14,670	Gas, house.	Grumell.
Yorkshire :									
Beeston	83·8	5·5	1·5	1·5	7·7	38·0	15,050	Steam, household.	,,
Parkgate (Nr. Rotherham)	82·3	5·2	1·7	2·8	8·0	34·4	15,480	Gas, coking, steam (Hards).	Survey Paper No. 13.

Barnsley	84·8	5·1	1·6	0·9	7·6	33·7	14,920	Gas, coking.	—
Barnsley "Hards" . .	85·1	5·1	1·5	0·8	7·5	34·7	14,940	Household steam (Hards).	,, ,, No. 18.
Silkstone	86·3	5·2	1·6	0·9	6·0	34·0	15,470	Gas, coking, household (Hards).	,, ,, No. 25.
Haigh Moor	84·1	5·6	1·8	1·4	7·1	35·0	15,100	Household.	Grumell.
Notts. and Derby :									
Top Hard	82·5	5·5	1·8	2·0	8·2	38·2	14,730	Household, steam (Hards).	,,
Deep soft.	80·7	5·8	1·8	1·3	10·4	38·7	14,590	Ditto.	,,
Waterloo (Chesterfield) .	81·8	5·4	1·5	2·0	9 3	39·9	14,570	Household.	Rep. of Test on Freeman Retort, 1926.
Tupton	81·4	4·9	1·7	3·1	8·9	39·0	15,050	Household and steam.	Report F.R.B. 1920–1.
High Hazel	80·0	5·5	2·0	1·4	11·1	38·8	14,230	Household.	Grumell.
Deep Hard (Nr. Alfreton) .	83·1	5·2	1·8	0·9	9·0	37·7	14,800	Steam, gas, household.	Survey Paper No. 30.
North Staffs :									
Banbury Seven Foot . .	81·4	5·4	1·7	1·6	9·9	38·6	14,420	Household, steam, manufacturing.	Grumell.
Cockshead or Eight Feet Banbury	83·0	5·4	1·9	0·7	9·0	36·2	14,820	House, steam, gas mnfg.	,,
Great Row	81·4	5·5	1·9	1·2	10·0	40·0	14,490	Pottery, steam, household.	,,
Warwick, Leicester and S. Staffs :									
Warwick : Slate . . .	79·7	5·3	1·0	1·2	12·8	43·7	—	Non-caking, steam.	Tech. Paper No. 32.
,, Two Yard . .	80·5	5·5	1·4	0·7	11·9	39·6	14,190	Household.	Grumell.
,, Seven Feet. .	79·4	5·5	1·3	2·2	11·5	47 0	13,920	Household and steam.	,,
Leicester : Main (Ellistown)	74·5	5·7	1·5	2·8	15·5	39·7	—	Household, mnfg. (non-cooking).	Tech. Paper No. 16.
South Wales :									
Craigola	91·5	4·3	1·5	0·8	1·9	14·5	—	Steam.	*T.I.M.E.*, lxx, p. 99.
Pentre and No. 3 Rhondda (Llanharan)	83·9	5·2	1·5	1·4	8 0	36 4	14,780	Coking and gas.	Tech. Paper No. 10.
Peacock Vein (Swansea) .	92·5	3·5	1·2	0·9	1·9	5·0	—	Anthracite.	,, ,, No. 29.
Bristol and Somerset :									
"Parkfield Large Gas" (mixture of Hard Vein, Top Vein, Great Vein, Hollybush)	84·5	5·4	1·8	1·8	6·5	37·7	15,030	Coking and gas, household.	Survey Paper No. 12.
East Kent :									
Milyard	88·6	4·5	1·2	1·9	3·8	22·8	15,540	Coking.	
Seam H (Betteshanger) .	91·0	4·2	1·3	0·7	2·8	15·4	15,700	Steam.	

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* E. S. Grumell (Trans. Inst. Min. Engs., 1931, 81, 214–59.

Its analysis when dry is ash, 4·0; carbon, 62·5; hydrogen, 4·9; nitrogen, 0·4; sulphur, 0·2 per cent., and calorific value 10,080 B.Th.U. per lb.

New Zealand. The coals, which occur in both the North and South Islands, are of considerable importance. The main deposits are of lignitic character, but various gradations of bituminous coals, including coking and good quality steam coal to anthracite, are found. Large quantities of steam coal were at one time shipped for Admiralty use in the East.

The Dominion Laboratory of the New Zealand Department of Scientific and Industrial Research is gradually collecting and publishing comprehensive data regarding the occurrence and properties of New Zealand coals and lignites. Bulletins 3, 8, 10, 14, 20 and 39 all deal with coal. In addition coal resources or properties are dealt with in the following: N.Z. Parliamentary Paper D–2, appendix C. 1926, W. P. Evans, *N.Z.J. Sc. and Tech.*, 1924, 2, 79.

The analyses of certain of the important coals are shown in Table XXI; the analysis of a typical lignite has been given on page 71.

TABLE XXI

COMPOSITION OF NEW ZEALAND COALS

	Volatile matter.	Ash.	Carbon.	Hydrogen.	Nitrogen.	Sulphur.	Oxygen.	Cal. Value B.Th.U. /lb.
Semi-Anthracite:								
Paparoa Mine.	16·8	4·9	84·6	4·4	0·7	0·3	5·1	15,000
Bituminous:								
Brunner Mine.	37·0	5·6	78·6	4·9	0·9	2·3	7·7	14,500
Millerton Mine	34·6	3·5	81·1	5·3	1·0	2·9	6·2	14,400
"Blackball".	50·0	0·2	78·2	5·9	0·9	4·4	10·4	13,300
Semi-Bituminous:								
Greymouth Mine	45·2	0·7	76·4	5·0	1·1	0·4	16·4	13,900

The coking coals such as Blackball are remarkable for their fusibility on heating and, when used for gas manufacture, must be blended with lignite to control this property. Some of them have also very low ash contents, 0·2 per cent.

India. The coals of India are of earlier (Triassic) formation than the coals of Great Britain. The most important fields are those of the Bihar and Orissa Province, one of which (Raniganj) extends into Bengal, and is the nearest source to Calcutta. The Central Provinces and Central India both contain a number of small coalfields of which the most important is the Rampur of the former field. In Assam seams have been found, ranging from 15 to 100 ft. in thickness, of reasonably good coal of appreciable coking power. In Burma coal and black lignites are both found, but are of doubtful economic importance.

In general, it may be said that India possesses large coal resources, but that comparatively little is known regarding the coal itself and that only these fields near industrial centres have been worked to any extent. The coal is normally of low coking power and high ash content. The inorganic matter is generally disseminated so that slack coal is of lower ash content than the lump coal. Analyses of certain Indian coals are given in Table XXII.

TABLE XXII

Average Composition of Pure Coal (i.e. moisture and ash free)

District.	Carbon.	Hydrogen.	Sulphur.	Nitrogen and oxygen.	Volatile matter.	Ash on dry coal.
Assam	81·1	5·8	2·9	10·2	46·2	3·6
Baluchistan . . .	79·8	5·9	3·2	11·1	—	—
Bengal:						
Klumardlubi . .	83·6	5·6	0·6	10·2	—	14·1
Jodepure . . .	82·3	5·6	0·3	11·8	—	9·2
Laikdih . . .	85·3	5·4	0·6	8·7	—	9·4
Central Provinces .	81·4	5·2	0·5	13·9	45·8	10·5

Canada. Canada possesses a number of coalfields which may be grouped roughly into four divisions:

1. The Maritime Provinces; comprising Nova Scotia and New Brunswick.
2. The Central Plains and Eastern Rocky Mountains—Manitoba, Saskatchewan, Alberta, British Columbia.
3. The Pacific Coast and the Western Mountains—British Columbia and the Yukon.
4. The Arctic-Mackenzie Basin.

The last named division consists wholly of lignite, but bituminous coal is found in each of the other three whilst anthracite is found in divisions 2 and 3.

The coals of the Maritime Provinces are similar to ordinary grades of English coal though, in the average, they have higher ash and sulphur contents. Most may be taken to be fair to good clean coals and excellent for domestic use.

The coals of the Central Plains and Eastern Rocky Mountains are of comparatively recent formation and many contain large quantities of disseminated mineral matter.

The Western coals are best developed in Vancouver and Graham islands; little is known of these coals except that from Vancouver island which is more or less normal bituminous.

TABLE XXIII

Composition of Canadian Coals (dry, ash-free coal)

	V.M.	C.	H_2.	N_2.	S.	O_2.
Nova Scotia	38·3	82·2	5·4	1·5	3·4	7·5
	44·0	74·7	5·2	0·9	8·0	11·2
New Brunswick	37·6	82·2	5·4	0·7	6·8	4·9
Alberta	33·0	84·3	5·0	0·6	1·2	8·9
British Columbia	27·6	86·4	5·0	0·6	1·4	6·6
Vancouver Islands	45·9	80·0	5·2	1·0	1·3	12·5
	35·1	83·2	5·0	1·0	1·1	9·7

Organizations working upon the development of Canadian lignites have been active for a number of years. These are, in Alberta, the Scientific Industrial Research Council; in Saskatchewan, the Government Province Committee; and in Ontario, the Ontario Research Foundation.

South Africa. Coal is distributed over a wide area, covering chiefly the Transvaal, Natal, and Orange Free State. In general composition the coals resemble those of India, being weakly-coking and of high ash content, although coking coal is found in limited quantity and pseudo-anthracitic coal in Natal.

The chief field in the Transvaal, indeed in South Africa, is the Witbank, regarding which detailed information is available in *Coals of the Witbank District*, by Graham and Lategan, Transvaal Chamber of Commerce, 1931.

The coal, and also that of the Orange Free State, is friable, producing a high proportion of slack on mining, and non-coking, and is good steam coal. The Natal coals are of better quality, but in many places are spoiled by igneous action.

Analyses of South African coal are given in Table XXIV.

TABLE XXIV

	C.	H.	S.	N.	O.	B.Th.U.
[1] *Natal:*						
Southern or Klip River Coal-field	86·6	4·8	1·7	1·7	5·2	13,600
Vryheid District	85·4	6·0	0·7	2·2	5·7	15,550
[2] *Transvaal:*						
Witbank, No. 1 seam	84·6	4·7	0·7	1·9	8·1	15,100
„ No. 2 seam	82·3	5·4	1·4	1·9	9·0	—
„ No. 4 seam	80·0	4·6	1·6	2·1	11·7	—

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[1] F. A. Steart, 3rd Empire Min. and Metall. Congress, S. Africa, 1930.

[2] Hall, J. Chem., Met. and Min. Soc. of S.A., 1930.

A Fuel Research Institute was started in 1930 to carry out research and survey work upon South African coals, but no results have yet been published.

In the other African colonies coal is found in Rhodesia, Nyassaland and Nigeria, the first and last fields being of considerable economic importance. The Udi coal of Nigeria is lignitous and disintegrates rather badly on weathering. Its analysis is: carbon, 81·4; hydrogen, 6·1; sulphur, 0·9; nitrogen, 2·1; oxygen, 9·5 per cent. Calorific value, 14,180 B.Th.U; all calculated to dry, ash-free coal.

PHYSICAL PROPERTIES OF COAL

Specific Gravity and Stowage Capacity. The specific gravity of coal is dependent upon two variables—the character of the combustible portion and the proportion of ash; the latter being of much higher density than the coal substance, and consequently exercising considerable influence on the specific gravity of the whole coal. The specific gravity varies between 1·27 and 1·45; only in exceptional cases will it fall outside these limits. On an average, anthracite is from 10 to 15 per cent. denser than bituminous coal.

The stowage capacity, or number of cubic feet per ton, will depend upon the specific gravity and size of the coal (relation of air spaces to solid).

Technical Data on Fuel (Brit. Nat. Ctee. of World Power Conf., 1932) give the following:

Anthracite	55–60 lb. per cu. ft.
Bituminous coal	50–55 „ „
Steam coal	50–55 „ „

The size of the coal has an important effect on its stowage capacity, for example:

2–1 in.	41·87 lb. per cu. ft.
$\frac{1}{2}$–$\frac{1}{4}$ in.	40·46 „ „
$\frac{1}{8}$–$\frac{1}{16}$ in.	38·61 „ „
$\frac{1}{32}$–0 in.	36·63 „ „

These figures are for dry coal and moisture has a considerable effect, giving an optimum low density in the case of coal slack at 8–10 per cent. moisture.

Moisture %.	lb. wet coal per cu. ft.	lb. dry coal per cu. ft.
0·9	49·0	48·6
8·3	41·7	38·3
11·5	43·6	38·6
14·9	47·6	40·5

Coherence. The resistance to breakage on handling is a most important factor; coals of otherwise excellent character are sometimes so soft that they are broken down during transport, with the production of so much small coal as to detract seriously from their value. Durham coking-coals are of this friable character. The waste in mining such coals is also great, and much of the small can be utilized economically only by briquetting or in producers. In shipment by older methods of tipping great crushing frequently results, which besides giving so much small coal, has a most important influence on the liability to spontaneous ignition. More recent methods involve the use of anti-breakage devices.

Lump coal tends to break down if stored for any length of time; some black lignites disintegrate in a short time completely to powder. The U.S. Bureau of Mines have developed a "slacking" test for coal in which a measured quantity of graded coal is alternately wetted and dried under standard conditions and the formation of undersize measured by screening. This test is likely to have wider application.

Thermal Properties. Calorific value is obviously one of the most important properties of a fuel. Methods of determination and calculation from analysis are described in Chapter XVIII. Until recently many of the published calorific values were open to question owing to the faulty methods of determination used. Now it is becoming recognized that the only reliable means is a calorimeter of the bomb type and standardized conditions. In considering calorific values of coal from the same source it is often of value to calculate the calorific value to the dry ash-free fuel and to use this value as a check. All consignments of the same coal should conform to the same dry ash-free calorific value, although small variations may occur in mixed consignments.

When coal is carbonized as in gas or coke manufacture the thermal changes involved (heats of reaction) are small. The complex bodies in the coal are broken down to simpler bodies in the products of carbonization, and since there is a difference in the heat of formation of the original and final bodies, the distillation is accompanied either by an evolution or absorption of heat. Mahler and Euchène were the first to attempt to estimate the magnitude of the thermal changes, the former by determining heats of combustion of the coal and of proportionate amounts of products, and the latter by preparing a thermal balance of a large scale carbonization. In more recent years the tendency has been to carry out experiments in specially designed calorimeters. References to three of the more important papers are given below.

In nearly all cases the thermal effect is small and variable, exothermicity or otherwise depending on the temperature of carbonization. In general, it may be said that peats, lignites and younger coals are more exothermic than the older coals, exothermicity apparently being somewhat connected with the oxygen content. Strache and Grau quote the following figures in calories per gm. for carbonization at 700° C.:

Wood	+ 168 to + 323 cals.
Lignites	+ 103 to 112
Brown coal	+ 25 to + 98
Bituminous coal	+ 30 to − 57

Below 600° C. some coals are exothermic and some endothermic, but above that temperature there is a general tendency towards endothermicity which is more pronounced above 800° C. The difficulties of experimental determination of definite values are very great and cannot readily be eliminated. They rather tend to show that the amount of labour necessary in this determination is out of proportion to the reliability of the results obtainable.

Terres (Bituminous Coal Conference, 1928) has also provided figures for the "coking heat" of coal. The "nett coking heat" is the number of calories required to convert 1 kg. of coal at 20° C. into coke at a definite temperature, including the energy in cals. corresponding to the external work performed by the distillation products. The "gross coking heat" includes the radiation loss from the ovens and the sensible heat content of the flue gases. The temperature normally adopted is 1000° C. The "heat of decomposition" is the net coking heat at the temperature in question minus the sensible and latent heat content of the coke and volatile products, and the heat equivalent of the work performed by these products against the atmosphere. In exceptional cases this heat of decomposition may vary from + 110 at 930° C. to − 75 cals. at 1010° C. Such a coal would require a long coking time. The net coking heat varies between 450 and 200 cals. per kg. of air-dried coal. Coking heats are highest in the case of coals having a high endothermic heat of decomposition The more exothermic the decomposition, the lower is the coking heat and the more endothermic the decomposition, the higher is the coking heat. When the heat of decomposition is zero the normal coking heat is approximately 325. The time required for coking coal in a coke oven can be calculated from Terres' data.

References: Davis, Place and Edeburn, *Fuel*, 1925, **4**, 286.
Strache and Grau, *Brenn. Chem.*, 1921, **2**, 97.
Terres and Meier, *Gas u. Wass.*, 1928, **71**, 451, 490, 519.

Specific Heat. The specific heat of coal is of interest in connection with carbonization problems generally. Coles (*J.S.C.I.*, 1923, **42**, 425T) gives the following values for dry ash-free coal at normal temperature:

Fusain	0·21–0·22	gm. cals./gm./° C.
Anthracite	0·22–0·23	„ „
Bituminous coal	0·24–0·26	„ „

In the case of coke Terres and Schaller (*Gas u. Wass.*, 1922, **65**, 761 *et seq.*) have shown that the specific heat varies with the ash content and gives values of which the following are typical:

t° C.	Mean sp. heat in cals./gm./° C.	
600	0·325–0·00081A	where A = ash per cent.
1000	0·382–0·00135A	

Thermal and Electrical Conductivity. Terres has also provided formulæ for the mean thermal conductivity of certain coals between 0 and *t*° C.—*t* being the temperature of carbonization.

For coking coals giving a coke of high density (low porosity)

$$k = 0{\cdot}0003 + 0{\cdot}0016 \times \frac{t}{1000} + 0{\cdot}0016 \times \left(\frac{t}{1000}\right)^2.$$

For gas coals giving a coke of average density

$$k = 0{\cdot}0003 + 0{\cdot}0013 \times \frac{t}{1000} + 0{\cdot}0015 \times \left(\frac{t}{1000}\right)^2.$$

For gas coals giving a spongy coke

$$k = 0{\cdot}0003 + 0{\cdot}0013 \times \frac{t}{1000} + 0{\cdot}0010 \times \left(\frac{t}{1000}\right)^2.$$

Processes have been suggested for the electrical carbonization of coal, in which case the conductivity or specific resistance of coal and coke is of special interest. A certain number of determinations of resistance have been made, but the values appear to vary within very wide limits and can as yet be accepted only with reserve. Fischer gives a value for bituminous coal of 5×10^7 ohms and Sinkinson gives a value of 4×10^6 and states that fusain has a very much lower value, 362 ohms. These values are quoted per c.c.

Solubility. Organic solvents are capable of dissolving coal in part, the amount dissolved depending upon the solvent and varying from about 0·1 per cent. with cold benzene to 47·3 per cent. with boiling quinoline. The most complete solution is assured in any solvent by acting upon finely divided coal at the boiling-point of the solvent or under pressure. Solubility in solvents has been made use of in separating constituents from coal which confer special properties such as coking power upon the coal. The two most commonly used have been pyridine at 118° C. and benzene under pressure at 275° C. The solubility of coal in pyridine varies with the type of coal from 7·5 to 42 per cent. and with benzene under pressure from 3·5 to 21 per cent. Further information regarding the properties of the extracts obtained is given in Chapter III. The effect of other solvents also varies with the type of coal. The more important of these are: acetone up to 3 per cent., aniline up to 12 per cent., phenol up to 35 per cent., tetralin up to 45 per cent., alcohol, carbon disulphide and ether all less than 1 per cent.

Further information upon the action of solvents is given by Bakes (Fuel Research Technical Paper 38).

Softening or Melting-point. When a coking coal is heated it passes through a series of stages, softening, swelling, setting and shrinking. The softening stage may be due to the liquefaction of the soluble fractions and is described variously as softening, melting or fusion of the coal. The temperature of inception varies with the type of coal and increases with the maturity of the coal. Charpy and Durand quote temperatures varying from 395–550° C., but Audibert prefers 320–400° C. The latter has shown that the value observed may vary with factors such as rate of heating, for example, in a parabituminous coal slow heating at a rate of 1° per minute gives a melting-point of 365° C., whereas rapid heating gives a figure of 325° C.

The relation between softening temperature and the temperature of rapid evolution of gases is of importance in affecting the type of coke produced on heating and in determining the best conditions under which a coal or blend of coals should be carbonized to give the best results.

Grindability. The behaviour of coals on grinding has become of importance in connection with the production of pulverized fuel, where the coal is reduced in size so that 90–95 per cent. will pass a 240 B.S.I. sieve. On grinding, all coals give particles of the same irregular shape, but the particles from air-swept mills have generally a rounded appearance, as distinct from the sharp edges seen in particles from the other mills. Wide variations are possible in the power required to reduce different types of coal to the same degree of fineness, but exact data are not yet available. It has been suggested that from this point of view bituminous coals increase in hardness up to the stage of 15 per cent. volatile matter and that the carbonaceous and anthracitic coals of lower volatile matter are progressively easier to grind. Grindability similarly increases with increase of volatile matter above 14 per cent., but exceptions occur in that durain coals are considerably harder than bright coals. In the grinding of coal it is accepted at present that Rittinger's law holds that the rate of increase of surface is proportional to the power applied in grinding. Coals could be compared on this basis if it were not for the fact that the power applied in grinding may be a very small percentage of the total power used by the mill.

In grinding coal to the necessary degree of fineness it is, of course, obvious that a large proportion of the coal will be very much finer than the upper limit. It may be taken that 30 per cent. of pulverized coal has a smaller particle size than six μ, i.e. one-tenth of the size of the largest particle.

CHAPTER VI

TREATMENT AND STORAGE OF COAL. BRIQUETTES. POWDERED COAL. COAL-OIL SUSPENSIONS

PREPARATION OF COAL

A small proportion of the coal mined is sold directly without further treatment (run-of-mine coal), but by far the greater proportion passes through some form of treatment before being marketed. Such treatment may consist of (1) separation of types of coal, (2) grading into size, (3) washing or cleaning, (4) mixing.

In a thick coal seam there may be more than one type of coal, i.e. brights and hards, and these may be brought to the surface separately. Similarly, sections of the seam which are high in ash or sulphur content may be kept separate. Grading consists of separating the coal into fractions of different size, each size being suitable for a specific purpose. Washing and cleaning consist in removing from the coal extraneous dirt introduced as pieces of the roof or floor, or dirt bands, imperfectly separated by the miner. Finally, mixing or blending is used to modify the properties of coal to suit one purpose. It should be realized that screening is also a mixing operation if a number of seams are being worked at one colliery, since one screen size will contain varying proportions of the coal from each seam.

Coal grading is to-day of the utmost importance. Coal cleaning, although not so important if clean seams are being worked, is important for small coal and will increase in importance as the thicker coal seams become worked out.

The first operation in dealing with coal at the surface is preliminary screening.

The chief requisite of the screening plant is that it should require little attention, that it should produce as little breakage of the material as possible, that it should be uniform across its surface and that the screen apertures should not tend to clog. Screening plant consists of several types, revolving screens, shaking screens and vibrating screens and the apertures in the surface may be either round or square holes. In screening, the shape of the coal and dirt is of importance and the greatest accuracy in screening is achieved when dealing with large dry coal on a vibrating horizontal screen, the material containing no flat pieces. The most common type of screen, however, is the longitudinal belt screen in which the angle of inclination is about 45°. The capacity of a 6-ft. screen of this type operating on 1½-in. coal, is about 100 tons per hour.

After screening, the large coal (over 3½ in.) is passed over picking belts where the foreign material is removed by hand. On a 100-ft. belt, six boys can pick as much as 100 tons of coal per shift.

The smaller coal may be sold without further treatment or it may be cleaned and sized carefully. In 1931, 66·7 million tons of this coal was cleaned, representing 30·4 per cent. of the coal mined and perhaps 70 per cent. of the small coal available. In 1927 the percentage was only 20·5. The 1931 coal was cleaned as follows:

By washing process	59·4	66·7 million tons
By dry cleaning	7·2	
By froth flotation	0·1	

Cleaning processes depend chiefly upon differences in specific gravity between clean coal and dirt, the specific gravity of coal being about 1·3, of shale about 2·5 and of pyrites over 4·0. Other physical properties which differ are coefficients of friction, resilience, shape and surface tension. Density differences are the most important and coals can be assayed for cleaning purposes by density separation, using mixed liquids of different densities for floating off the coal in fractions. Such liquids may be mixtures of carbon tetrachloride and toluene, or solutions of calcium chloride. An example of such a separation is shown in Table XXV of a coal containing 15·3 per cent. of ash.

TABLE XXV

Flotation of Coal

Sp. Gr. of liquid.	Floating material.		Sinking material.	
	% yield.	ash %.	% yield.	ash %.
1·25	5	0·8	95	16·0
1·30	65	2·4	35	39·3
1·35	75	3·1	35	51·8
1·40	79	3·8	21	58·5
1·50	82	4·5	18	64·1
1·60	85	5·6	15	70·0

If clean coal of less than 5 per cent. ash were required it would be necessary to "cut" at 1·50 sp.gr. in which case the yield would be 82 per cent. of coal at 4·5 per cent. ash. The performance of a washery would be judged in terms of how closely it could work to the assay results. These results can also be expressed graphically, as shown in Figure 5.

The clean coal and dirt curves are self-explanatory. The increment curve shows the ash content of the coal corresponding in specific gravity to the " cutting " point. The dotted line represents the " cut " selected from the tabulated results.

In one commercial process (Lessing) simple gravity separation is used, the liquid being a solution of calcium chloride in water. In most commercial washing processes, however, the principle employed is the rate of settling of the particles in a fluid, such as water or air. This rate reaches a constant or terminal velocity when the resistance of the fluid equals the weight of the particle. Neglecting shape, increase of size or density affects the terminal velocity. The principle is applied directly in upward current washers of which the best known is the Draper Tube. If the velocity of the upward current of water is slightly greater than the terminal velocity of the coal, the heavier dirt will sink and the clean coal will be carried forward in the water stream. The great difficulty with this type of plant is the obvious necessity for close sizing. In practice the size range cannot be more than 2 to 1. For this reason this type of plant has not a wide application in coal cleaning. Commercial washers may be divided into classes as follows :

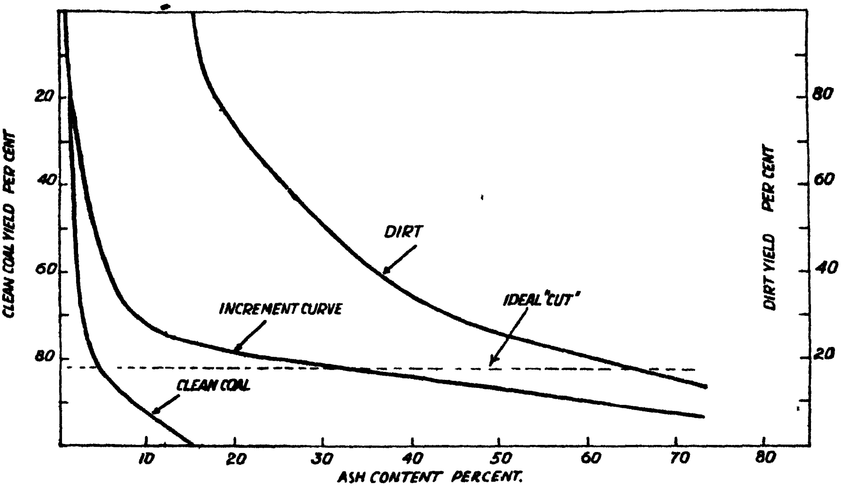

FIG. 5.—Typical Washability Curves.

1. *Wet Processes*, (i) Gravity separation, (ii) Upward current washers, (iii) Trough washers, (iv) Jigs, (v) Concentrator tables, (vi) Froth flotation ; 2. *Dry Processes*, (vii) Air tables, (viii) Spirals, (iv) Berresford process.

In trough washers the coal is caused to flow down a launder in such a manner that stratification according to density takes place and mechanical separation becomes possible. In the Rheolaveur type the trough contains slots specially arranged to separate the dirt.

In Jig washers water is caused to pass upwards through a bed of coal (1 ft. thick) in a series of pulsations so as to create stratification. The lighter clean coal passes over a sill on to screens, while the dirt is discharged through the gates in the side of the box. This type of washer is the most favoured in this country for general operation. Figure 6 illustrates the wash-box of a British Baum Jig washer where the pulsations are given by compressed air.

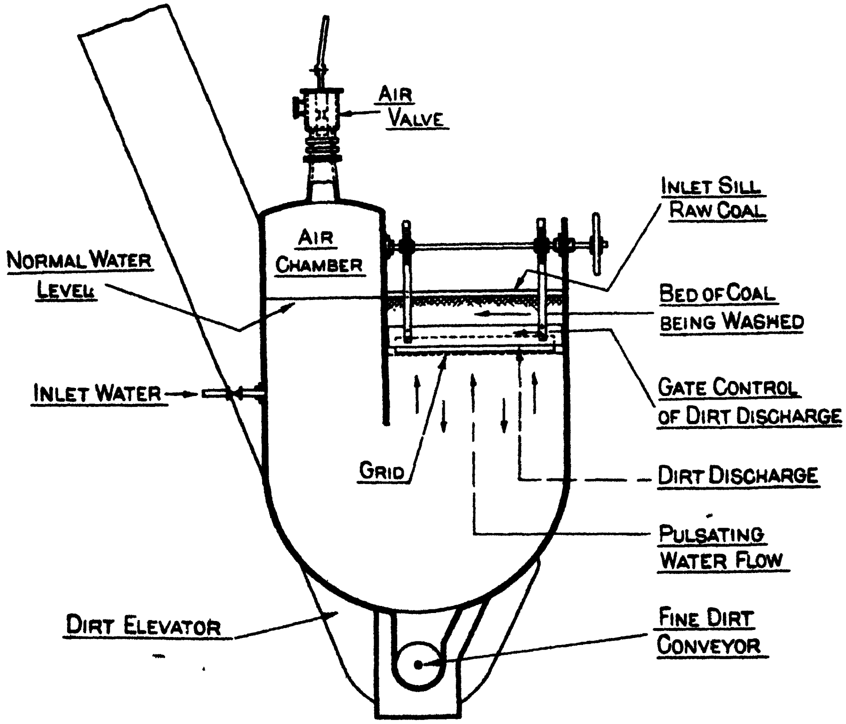

FIG. 6.—Diagrammatic Section of British Baum Wash-box.

Concentrator tables are identical in action to those used in ore dressing. The table, which is fitted with wood riffles, is oscillated lengthwise while coal is fed to the top and water flows transversely. The combined action of the oscillations and the water stratifies the coal, the clean coal riding over the riffles and the heavier dirt being carried along the riffles to the far end.

Air tables are similar in action, the table being perforated and the air coming through from below. The specific importance of air tables and other dry cleaning processes is their ability to produce products which do not have the disability of high moisture contents.

It is generally recognized, however, that they are not quite so efficient in that the ash content of the clean coal is higher.

Froth flotation processes are used only to a very limited extent and for further particulars regarding this and the processes outlined above, reference[1] to Chapman and Mott (Chapman & Hall, London, 1928) is recommended.

In all cleaning processes the fine coal (less than $\frac{1}{16}$ in.) is the cause of much trouble. In wet processes, it forms a slurry which requires special auxiliary plant for its separation from the washery water since this has to be kept below a certain percentage of solids in suspension. In dry processes it necessitates the installation of elaborate dust-collecting plants. At many collieries, the coal before cleaning is dedusted to avoid this complication, the dust being sold for such purposes as pulverized fuel.

COMBUSTION OF COAL AND FORMATION OF SMOKE

The combustible elements of coal consist of carbon, hydrogen, and a portion of the sulphur, and when their combustion is properly completed the flue gases should contain only carbon dioxide, water vapour, and sulphur dioxide, in addition to the large volume of nitrogen which accompanied the oxygen of the air used in the process. The theoretical amount of air for fuel of any given composition can be calculated readily, but in practice it is found impossible to get the best results without using a considerable excess of air.

The combustion of coal is in practice a compromise; it means striking the best balance possible between losses of heat units through incomplete combustion on the one hand, and losses through heat units carried away in the flue gases by an excessive supply of air on the other hand. The calculation of the theoretical supply of air and the losses through the last-named causes are dealt with fully in Chapters I and XIX. Here, it is only necessary to deal with the question of incomplete combustion, more particularly in its relation to the formation of smoke.

Theoretically, an average bituminous coal requires 11 lb. of air or 140 cu. ft. per lb. but perfect combustion under the best conditions of grate firing cannot be attained without 20 per cent. excess, say 170 cu. ft. Incomplete combustion may exist without visible evidence when carbon is partly burned to carbon monoxide instead of the dioxide, and when hydrocarbon gases escape unburnt. Visible evidence of incomplete combustion is given by the formation of smoke. When carbon is burnt to carbon monoxide, out of the possible 8130 calories per kilogram (or 14,650 B.Th.U. per lb.) only 2490 calories (or 4480 B.Th.U.) are actually produced. With escaping hydrocarbon gases the losses may also be very high, since these gases have a very high calorific value. The conditions favourable to the formation of carbon monoxide are a thick fuel bed (see Theory of Producer Gas Reactions, p. 275) and insufficient supply of air over the bed. The 20 per cent. excess air will ensure against both these losses with reasonable management, but by no means ensures absence of smoke, other very important factors being involved.

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[1] See also Coal-cleaning Conference, *J.S.C.I.*, 1927, **46**, 229T.

Smoke is formed from the distillation products of the coal, which, owing to imperfect systems of firing and furnace arrangements, escape before combustion is completed. Obviously, the smaller the amount of volatile matter commensurate with free burning properties, the less the liability to smoke, which explains the special characteristics of Welsh smokeless coals. The production of smoke is best understood by following the sequence of events when a bituminous fuel is hand-fired. A layer of white-hot solid carbon is on the firebars, with probably an excess of highly heated air passing through; coal is thrown in and partially checks the hot air supply over a portion of the grate; there is a local sudden cooling due to cold coal and the evaporation of moisture from the coal, and a rush of cold air through the open door produces general lowering of temperature over the grate. Possibly the interaction between steam and carbon, which absorbs heat no matter whether producing carbon dioxide, or the monoxide together with hydrogen, also exercises a minor cooling effect. Almost immediately the destructive distillation of the coal sets in, and with small coal this may be extremely rapid, with the evolution of large volumes of combustible gases and vapours over a small interval of time.

A ton of bituminous coal will yield 11,000 cu. ft. of gas, and in addition large volumes of vaporized products (the tars resulting in gas manufacture), giving a total which may be taken approximately at 13,000–14,000 cu. ft. per ton, or about 6 cu. ft. per lb. of coal charged. With a moderate charge of 40 lb. of coal this means that some 240 cu. ft. of gases are set free; on an average each cubic foot will require 3 cu. ft. of oxygen or 15 cu. ft. of air, so that the air supply for complete combustion of these volatile products must be 3000 cu. ft.

For the perfect combustion of these gases there must be obviously no deficiency in oxygen; further, that as intimate a mixture as possible of combustible gas with the necessary oxygen must be made; and lastly, that as high a temperature as possible shall be maintained, otherwise combustion will be checked and smoke formed. The necessity for the last two conditions is well illustrated by the actions with a paraffin lamp. Lighted up without the chimney the flame extends itself greatly in its effort to obtain the necessary oxygen; owing to this diffusion it becomes so cooled that smoke is formed freely, and the flame towards its edges is of a red colour with little luminosity, due to its low temperature. With the chimney the air supply is directed properly on to the flame, which is greatly reduced in size, the increase in the intensity of its combustion is manifest by the disappearance of the red colour and the increase of luminosity, and no smoke is formed. If the conditions of combustion of coal under any boiler fail in one of these points, smoke will result.

The supply of the large number of cubic feet of air during the first few minutes after firing is the first consideration. It is well known that keeping the door open for a short time, or providing for sufficient air inlet through suitable louvres in the door arranged so that they may be gradually closed, is effective in preventing smoke, if the other conditions named are satisfied, but a good draught is essential. When a boiler is working for some time below its maximum, the chimney damper being partly in, there may be difficulty in getting the requisite air over the grate unless an ash pit damper is provided. Obviously, the provision of sufficient air at any and every moment will be simplified and better opportunity of proper mixture ensured if there is no rush of combustible gases at any time. This will be best attained by a continuous feed of fuel, as with mechanical stokers, or, if necessarily intermittent, as in hand-firing, by the adoption of either a " coking " or " alternate " system of firing. By charging the fuel on a dead plate just inside the door with suitable air admission above the grate, distillation proceeds slowly, the products passing with the necessary air over the highly incandescent fuel on the bars, where they meet with further excess of air at high temperature. When distillation is completed the coked mass is distributed over the grate. The objection to the method is mainly that it is frequently impossible to burn the quantity of fuel requisite for maintaining steam, but it is certainly the most scientific method of hand-firing.

Alternate firing may be either in sections over the front and back of the grate, or sections to the right or left. In either case proper admixture with air and maintenance of the necessary temperature are assured, if the furnace construction is a proper one. Necessarily the more frequent opening of the doors with the accompanying losses through excess air are involved, and success with either coking or alternate systems is dependent on the skill of the fireman.

The question of mechanical stokers and their operation is outside the scope of the present volume, but brief reference to one or two points may be made. All are dependent upon the principle of practically continuous feed, with its advantage of uniform evolution of the smoke-producing elements. It is therefore easy to adjust the air supply so that, whilst ensuring complete combustion, no unnecessary excess is employed, whereby the highest efficiency is secured, providing the arrangement is such that towards the back of the grate air is not able to pass freely in through a residue of nearly completely consumed fuel. The amount of fuel which can be burned per square foot of grate area is higher under these uniform conditions, and consequently the duty of the boiler is increased, which often leads to a reduction in the number requisite for a given output. Again, it is frequently possible to use a cheaper grade of fuel than with hand-firing, and saving in labour costs is also effected.

The second essential for smokeless combustion is efficient mixing of the gases and air. This will reduce the length of the flame and increase its calorific intensity, enabling the combustion to be completed before an inordinate space, with possible contact with cool surfaces, has been traversed. A suitable direction to the in-going air may be given at the door by plates, etc., and sometimes a steam jet or jets can be effectively employed. In an internally fired boiler there is seldom any difficulty as regards mixing, owing to the rapid sweep of the gases and air towards the firebridge.

The third condition of maintenance of a high temperature is of equal importance to the supply of sufficient air. In the domestic fire there can be no question of any deficiency of air, but its smoke-producing powers are obvious and are due primarily to cooling, and to a minor extent to insufficient mixture. In boiler practice it is essential that the mixture of gases, vapours, and air in a state of incomplete combustion shall not come in contact with any surface at a comparatively low temperature, such as that at which the boiler plates and tubes are. With an internally fired boiler there must be sufficient space between the grate and plates, which will be governed largely by the character of the fuel to be generally employed, that is, its percentage of volatile hydrocarbons. With cross-tubes it is impossible to avoid this contact. Beyond the grate and divided from it by a firebridge a capacious combustion chamber of firebrick reduces the speed of the gases, and enables combustion to be completed before the gases are drawn into the flues. In a water-tube boiler the incompletely burned mixture must be prevented from contact with the lower tubes, either by suitable arches, baffles or fireclay covering to the tubes.

The partial failure of one or other of these conditions will exercise an important influence on the character of the smoke. On distillation at low temperatures coal yields chiefly tar-forming bodies and rich hydrocarbon gases, while at high temperatures, after the former have distilled off, other bodies break up, yielding gas very rich in hydrogen. The tarry bodies (existing partly as heavy vapours and gases in the furnace, and possibly even as liquid vesicles) and the hydrocarbon gases will differ very much in their combustion. It will be more difficult to ensure complete admixture of the former with air, especially if liquid vesicles are present, and they will escape with very little alteration beyond combustion of the more volatile portions, giving a *brown* tarry smoke. The hydrocarbon gases will mix more readily with air, and if intensity of combustion is maintained, will undergo complete combustion, but should this be checked by cooling, dense clouds of *black* smoke, consisting largely of free carbon, will be produced. Should this free carbon once be produced no excess of highly heated air will cause its combustion, a result which has frequently given trouble in burning liquid fuel. The high-temperature gaseous products of distillation, consisting mainly of hydrogen, will offer no difficulties in combustion; it is the low-temperature products, given off with a rush on firing, and the character of these products which are wholly responsible for smoke. Deficiency of air and improper mixing will result chiefly in brown (tar) smoke with little free carbon; checking of combustion will be the primary factor in the production of black smoke.

A great deal is made of the losses of fuel due to the formation of smoke, and results are quoted frequently showing the great saving in fuel which has resulted when the boiler plant has been remodelled, primarily to overcome the smoke difficulty and to satisfy the local authority. These very great savings are, however, dependent far more upon avoidance of heavy losses through excess air and bad flue gases than upon heat units saved by utilization of the smoke. Under the old system very large excess of air was general in the attempt to avoid dense smoke; with the modernized system it has been possible to reduce greatly the air supply and still attain much better combustion. What percentage of the heat units in the fuel actually escapes in smoke it is impossible to ascertain directly. From an approximate estimate by Cohen and Ruston (*Journ. Gas Ltg.* 1910, **112**, 201), the amount of soot collected by filtration of the air in the manufacturing district in Leeds is equal to 0·5 per cent. on the coal consumed. They state the quantity to be over 5 per cent. for domestic fires, and therefore that the estimate for industrial smoke is probably low. The composition of the combustible portion showed 85 per cent. carbon and 15 per cent. tarry matter, and on this basis it would have a calorific value of 8500 cals. (15,330 B.Th.U.). Allowing 1 per cent. of the coal escaping as smoke, with average bituminous coal the percentage of heat units escaping would be 1·2 per cent. By raising the carbon dioxide in the flue gases only 1 per cent., twice this saving of heat units could be effected, and fortunately the means taken to overcome the smoke trouble, usually the installation of mechanical stokers and careful regulation of air, are just those which enable better economy to be obtained through generally better conditions of combustion, and the economy found is ascribable only to a limited extent to heat units recovered from the smoke itself.

Harmful and objectionable in every way as smoke is, it must not be overlooked that the sulphur dioxide which accompanies it is one of its most injurious features, and that whilst the visible smoke may be reduced or abolished, this sulphur dioxide will still pass into the atmosphere.

The erection of very large electricity generating stations, where large quantities of coal are burnt daily, has directed attention to the evils resulting from the discharge of very considerable quantities of sulphur dioxide into the atmosphere. This gas, even highly diluted, is rightly regarded as inimical to the population and destructive to vegetation. Moreover, it is brought down by rain as dilute sulphuric acid, the sulphur dioxide in the presence of the moisture being oxidized to sulphuric acid.

According to the 17th Report on Atmospheric Pollution (*Dept. Sci. Ind. Res.*) the amount of sulphur, as sulphur trioxide (SO_3) collected at the thirteen stations in the London area amounts to some 35–36 tons per square mile per annum; at a station in Liverpool over 68 tons. W. C. Reynolds (*J.S.C.I.*, 1930, 168 T.) reports extensive investigations of the air in London and found that at Plaistow (E.) in the winter there were 400 volumes of sulphur dioxide per 1000 million volumes of air; in the summer the quantity was one-fifth of this.

To deal with the flue gases from these large coal-consuming plants washing with water sprays has been adopted. S. L. Pearce (see *Eng.*, 1930, p. 312) states that with a 40,000 H.P. boiler, a gas velocity of 3 ft. per second, and contact time of twelve seconds, 20 tons of water per ton of coal will almost entirely remove the sulphur dioxide, and weak alkaline solutions are more effective. Sulphur dioxide is not too readily taken up by water and H. F. Johnstone, of the University of Illinois, claims that a very weak solution of manganese salts catalyzes the oxidation of the SO_2 into SO_3, when only 1·25 tons of water per ton of coal will remove the latter.

THE DETERIORATION, HEATING, AND SPONTANEOUS IGNITION OF COAL

These phenomena are all intimately connected with each other, the degree to which spontaneous oxidation of the coal proceeds alone determining whether simple deterioration in quality results, or whether overheating and finally spontaneous combustion are set up.

It is well recognized that freshly mined coal frequently undergoes a rapid loss in calorific value during the first week or two after its removal from the pit, and old pillars of coal in the pit have been found to have an appreciably lower calorific value than the coal as freshly cut from around them. Parr and Wheeler found that American bituminous coals lost from 1·3 to 3·4 per cent. of their calorific value in ten months, but that the loss is confined nearly wholly to the first two or three weeks. Such loss usually is ascribed to escape of hydrocarbon gases (methane, etc.), which are of relatively high calorific value, but the loss in most instances appears to be greater than is probable from such causes alone, and absorption of oxygen must be a contributing factor.

Absorption of Oxygen by Coal. Many bituminous coals contain unsaturated compounds which are capable of absorbing oxygen from the air. For this absorption to take place the physical condition of the coal will be the primary controlling factor ; its size, as governing the relations of surface to mass ; its hardness ; its porosity. Demstedt and Biinz (abs. *J.S.C.I.*, 1908, 929) show that absorption is dependent upon unsaturated oxygen-containing compounds, that these compounds are not present in any quantity unless the coal has a high oxygen content, and establish their unsaturated character by the response of such coal to the iodine absorption test and Maumène test, as applied to oils containing unsaturated compounds. The work of Boudouard and others confirms this view, and also that by further oxidation the products are humic acid and similar substances. Freshly mined coal placed in air-tight vessels absorbs oxygen at first without the formation of carbon dioxide ; it is only at a subsequent stage that this gas is evolved, showing that a process of slow combustion is set up, the heat from which is usually disseminated rapidly.

In a very large number of cases these actions proceed no farther, but the practical results on the qualities of the coal are most important. Reference has been made to the loss of coking power of some coals on exposure to air and, above, to the loss of calorific value ; the ash is said to be raised, evidently through the escape of coal constituents as gases or vapours, the gas yield lowered, and more heat demanded for gas manufacture. When large stocks of coal have to be maintained, as in the gas industry, these results are of great importance. Grundmann has shown that Rühr coal gives from 1 to 7 per cent. lower gas yield after 14 days' exposure ; from 3 to 12 per cent. after 150 to 180 days, and from 8 to 17 per cent. after 370 to 380 days' exposure. With an English coal at the Königsberg gas works the following yields were obtained :

Coal as discharged . . .	10,870 cu. ft. per ton of dry coal
„ after 3 months . . .	10,815 „ „ „
„ after 7 months . . .	9,930 „ „ „

Gas coals are not necessarily strongly caking coals, so that it would be expected that after exposure of the coal the coke would be less coherent, that is, that the proportion of breeze would be increased.

That this is the case is shown by results from the Breslau gas works:

	Fresh screened lump.	Fresh unscreened.	Weathered.
Large coke	93·3	86·1	52·6
Small coke	4·4	8·8	18·9
Breeze	2·3	5·2	28·4

Storage of Coal. There is a general consensus of opinion that some deterioration ensues with most bituminous coals, which affects their value for practically all purposes. When large quantities have to be stored, the reduction of this to the minimum is obviously desirable, if it can be accomplished at a cost commensurate with the saving. The first idea would be the avoidance of oxidation by exclusion of air, either in air-tight chambers, which is impracticable, or by storage under water. Coal removed from water and properly drained should not contain more moisture than washed coals; but storage under water is probably only justifiable under exceptional circumstances.

Storage under conditions which limit the amount of weathering, which includes the effect of moisture and oxidation, is more practicable. Moist coal is primarily more readily oxidized, and water exercises a disintegrating action, especially in winter, so that the coal becomes more open and porous. When properly stacked in the open, whilst the outer portions are undoubtedly affected, this, on the whole mass, is not serious, especially if the outer pieces are of fair size. The smallest area exposed in relation to the whole mass will give the best results, but this entails deep stacks with accompanying liability to heating and ignition. Good results follow the use of covered stores for soft friable coals, but generally the expense entailed is proportionately high to the preservation effected. With hard coals the weathering is not great.

Spontaneous Heating and Ignition of Coal. Where oxidation proceeds to a more advanced stage it may lead to considerable heating and possibly spontaneous ignition of the coal. At one time heating was confidently ascribed to the oxidation of iron pyrites, but the evidence against pyrites playing more than a very minor part is overwhelming and this chiefly mechanical, assisting disintegration. The serious losses which may occur through spontaneous ignition in stores or coal cargoes render it necessary that the conditions through which heating may arise should be carefully studied, if proper measures are to be taken for its avoidance.

Modern views on the changes involved, largely based on the work of Parr and his collaborators (*Univ. of Illinois*), are, that after the coal has been broken out and the evolution of occluded hydrocarbon gases has practically ceased, the absorption of oxygen commences, which is accompanied by a slow rise of temperature, when the conditions of sufficiently rapid absorption (fineness of division chiefly) and prevention of escape of heat are present. It is not until a temperature of about 120° C. is reached that carbon dioxide and water vapour make their appearance, indicating that a slow combustion has started. Under suitable conditions the process accelerates until a temperature of 140° to 160° C. is reached, when the rate of increase of temperature becomes much greater, until between 200° and 275° C. a self-sustained process of combustion sets in with very rapid rise of temperature until the ignition point, which may lie between 300° and 400° C., is attained, when active combustion is set up.

It is evident that for coals to undergo this process certain chemical and physical conditions must exist. The chemical condition is the presence of unsaturated easily oxidized substances, but of the nature of these practically nothing is known. Demstedt and Biinz (*loc. cit.*) have proposed testing the finely divided coal by packing in a tube, with thermometer, passing carbon dioxide through the tube heated to 100–115° C. in an oil bath, to dry the coal, then raising the temperature to 135° or 150°, while dry oxygen is passed through at the rate of 2 to 3 litres per hour. Coals which heat up slightly above the bath temperature, and will heat up more rapidly and perhaps ignite on increasing the oxygen supply, are dangerous.

The physical conditions must be such that oxidation with accompanying generation of heat must be sufficiently rapid in relation to the cooling factors. Large surface—fineness of division—is essential to heating. It has always been noted that fires in coal cargoes start invariably under the hatchways, where there is great crushing, and that large coal never heats if free from smalls and particularly dust. For the heat generated by this oxidation to become serious it is obvious that the action must be cumulative, that is, that the heat shall not become dissipated to any great degree. It has been estimated that the heat developed amounts to 90 B.Th.U. per cubic foot of air participating. A solid mass of coal is of a low order of thermal conductivity, and, when broken up, the air spaces further greatly lower its conductivity. Given a sufficiently large mass of coal with generation of heat taking place some distance from the surface, the escape of heat is prevented and the temperature at the affected part will rise until the self-sustained stage of oxidation is reached, ultimately resulting in firing if the supply of oxygen is sufficient to sustain rapid combustion. If this is not the case oxidation will proceed only to the limit of available oxygen, the rate will fall practically to zero, and the heated portion gradually cool off.

Experience shows that a large mass of coal in which conditions are favourable is far more likely to heat and finally ignite than smaller masses. In the case of coal cargoes this is particularly noticeable, statistics over one period showing that whilst the casualties for cargoes between 500 and 1000 tons were 1 per cent., with cargoes of over 2000 tons they amounted to 9 per cent. Again, there is a safe depth to which a coal may be stacked without risk, but it does not always follow that shallow stacks are safe, and fires have occurred within a few feet of the surface in deep stacks. It is difficult to see that mass alone should have any effect, provided there is sufficient to properly heat-insulate a zone where conditions of size, etc., are favourable to heating; rather should it retard that free accession of oxygen essential to the process. The explanation of this apparent effect of mass arises most probably through the greater quantity of smalls and dust produced in handling these large quantities.

Another important consideration is the effect of moisture in promoting heating, and very contradictory opinions are held on this point, due doubtless to the lack of distinction between moist coal and wet coal. In the Report of the New South Wales Commission on Spontaneous Ignition (1900), there appears an account of experiments with two bins 21 ft. square loaded with the same coal, one kept dry and the other saturated from a hose until water ran off in a small stream. The dry coal heated, but the wet did not. The result was said to prove conclusively that dry coal was most dangerous, and that the view of the British Commission (1876), supported generally by evidence before other Commissions, that wet coal was most dangerous, should be abandoned. The experiment really proved only that when sufficient water was present to prevent appreciable access of oxygen to the coal surface, it would not heat. If the moisture present is not sufficient to exclude oxygen from the surface there is every reason for still believing that it will materially assist chemical action. Doane (*Eng. News*, 1904, **52**, 141) states that the amount of moisture in an air-dried bituminous fuel is a measure of the risk from spontaneous ignition, and that bituminous coal with over 4·75 per cent. is most dangerous. There is little reason, however, for believing that moisture *per se* can be such an important factor. In the oxidation of pyrites it plays undoubtedly an important part.

The prevention of heating and ignition in coals liable to these changes evidently is primarily dependent upon prevention of oxidation at any centre being sufficiently rapid to more than counterbalance the natural cooling effect of the surrounding masses of coal. It is only in places where the surface area of a considerable quantity of coal in relation to its mass is very great, that is, where there is an accumulation of fine and dust surrounded by sufficient material to give the necessary heat insulation without cutting off the supply of oxygen, that heating can ever arise. With larger coal slow oxidation of the exterior faces alone is possible, and beyond slight deterioration can do no harm; it is the accumulation of masses of small coal which must be avoided. In loading cargoes with the usual tips such accumulation under hatchways is unavoidable; the distribution of such crushed material has been suggested, but obviously this would be a matter of difficulty in the hold of a ship, and the adoption of more modern methods which lessen the crushing is the correct solution of the problem. In stacking coal this distribution can be conveniently arranged, and small coal amongst larger sizes checks to a great degree the access of air to the mass; further, by building up in sections, or simultaneously, in more than one stack, a period may be allowed to elapse before successive layers are added, so that the initial oxidation may have made considerable progress in the top layer before another is added.

The depth to which coal may be safely stacked is dependent upon many variables, and upon the nature of the coal. The normal height of coal stacks is from 12 to 16 ft., but certain coals which are not liable to spontaneous heating may be stacked even up to 30 ft. Such coals are Scottish and South Yorkshire steam coals, Midland hards and Welsh steam coals. Other coals such as those of Durham and Forest of Dean have to be watched closely, even when stacked to a height of 10 to 12 ft. Generally speaking, freshly mined coal is more liable to heating, and after coal has been on storage about nine months the stack may be regarded as quite safe. Sized coals of over single nut size are safest on storage, and coals containing an appreciable quantity of fines are the most dangerous. In some cases it is the practice to sieve out the fine material from coal to be stacked and place this over the surface of the stack to form a blanket and prevent air circulation. In building a stack a low boundary wall is an advantage, since it prevents circulation of air into the bottom of the heap. It is said to be an advantage to build a stack end to the prevailing wind. The general precaution is that as little breakage as possible should be caused during storage, since the freshly broken surfaces of coal are more liable to oxidation. The height to which a stack is built depends upon the above variations, but greater latitude may sometimes be allowed if a crane and grab are available, since by this means the coal in the neighbourhood of a fire may be more rapidly removed than by hand.

The question of providing ventilation to the coal in store is important. On the one hand, if air cannot penetrate with sufficient rapidity the oxygen gets slowly used up, the coal may heat a little, but will cool off slowly by conduction. On the other extreme, if the air supply could be sufficiently great, whilst oxidation would occur to the maximum extent possible for the temperature attained, the good air current would carry off the heat and again cool the mass. The whole difficulty in a stack or cargo is to provide this large excess of air, for if insufficient for any reason it will evidently promote ignition by freely supplying the necessary oxygen. It is a striking fact (1876 Commission Report), that in four vessels laden with between 1500 and 2000 tons of the same coals shipped at the same time at Newcastle for Bombay, only one arrived safely, and that the one in which no attempt was made at ventilation. It may be safely asserted that it is next to impossible to provide such adequate ventilation as to keep a stack or cargo cool, so that attention must be given to other methods indicated.

A careful record of the temperature in various parts of the coal should be taken by means of iron pipes bedded in, down which maximum recording thermometers may be inserted, and if the temperature is found to rise unduly, the upper layers should be removed. Any external source of heat, such as contact with warm pipes or bulkheads, must be carefully guarded against, since heat in the initial stages quickly results in the attainment of the dangerous heating stage. It is well recognized that a cargo shipped in the summer, especially after exposure to the hot sun, is far more liable to ignition for the same reason.

Below a certain temperature it would be expected that the rate of oxidation would be so slow as to be negligible ; it may be concluded, therefore, that there is an approximate minimum temperature at which action likely to develop dangerous conditions may occur. Davis and Byrne place this "zero" temperature at 77° F.

In conjunction with the Board of Trade investigations were made by the Fuel Research Station on the probable cause of outbreak of 336 fires which were reported during the three years 1925–8, and a Special Report—"Fires in Steamship Bunker and Cargo Coal" (No. 5. 1929) was issued.

Most of the fires occurred in bunkers, and more than 60 per cent. were attributed to external heating—from engine and boiler rooms, steam pipes, etc.

Leakage of air through the coal, with other conditions favourable, was responsible for others. Faulty ventilation, permitting air to pass through the coal, also falls into this category.

Another cause was reported to be loading fresh coal on top of coal which had been lying for some time in a bunker. The facts of ignition in such circumstances are well substantiated, but the reason is not easy to arrive at. It might well be concluded that such stale coal had already been oxidized beyond its danger-point.

The suggestions made in the Report for avoiding fires but reiterate what has been emphasized hitherto, namely, avoidance of unnecessary breakage and accumulation of " smalls," preventing access of heat from external sources (use of double walls with air space, efficient lagging of steam pipes, etc.), prevention of access of air through the coal, and trimming remaining old small coal towards the doors before loading fresh coal.

In view of the New South Wales results referred to above, it has been suggested that water from a hose should be played upon the coal accumulated beneath the hatchways when loading. It is estimated that 10 per cent. of water prevents heating, and assuming the coal as shipped contains from 2 to 3 per cent. of water, the additional water demanded would be 8 per cent. on approximately one-fifteenth of the whole cargo, equal to only a half per cent. on the total cargo (Threlfall, see *J.S.C.I.*, 1909, 759).

Lewes (*J. Gas Ltg.*, 1906, **94**, 33) recommended placing cylinders of liquid carbon dioxide at points where heating was probable, the cylinders being sealed with a fusible alloy melting at about 93° C., the valve being opened before the cylinder was placed. On rise of temperature the alloy would melt and allow the escape of the gas, which would quickly put an end to oxidation.

Further information upon the subject of spontaneous combustion of coal can be found in the papers by Stopes and Wheeler (Safety in Mines Paper 28, 1926) and by Davis and Reynolds (U.S. Bur. Mines Tech. Paper 409, 1928).

COAL BRIQUETTES (PATENT FUEL)

The necessity for finding a market for the small coal and slack of all types produced in mining, has led to considerable developments in the production of briquettes. In the mining of brown coal on the Continent, plant has been developed for the briquetting of the dried coal by pressure alone. This type of coal gives satisfactorily strong briquettes without the addition of a binder. The process has provided a large market for a fuel which would otherwise be difficult to apply commercially.

In this country where the slacks to be treated are either bituminous coal or anthracite, briquetting without a binder of some sort is not a commercial possibility on account of the high pressures of over 12 tons per square inch which are necessary. Although a certain amount of work has been done in this country, using coal in a fine state of division (85 per cent. below 200 mesh), and some success has been obtained as far as the strength and hardness of the briquettes, the heavy costs of the strong presses necessary have prevented commercial development, and in order to make strong briquettes from bituminous coal and anthracite, a binder is necessary. The most satisfactory for this purpose is pitch prepared either from wood, petroleum or coal tars, especially the latter. The proportion of pitch necessary can be reduced by fine grinding, but this is not normally done owing to difficulty in grinding and to fire risk. The pitch is usually passed through a disintegrator with the coal. The best type of pitch is a soft pitch which has a twist point of 55° C. Too soft a pitch becomes difficult to handle in warm weather and the briquettes made from it are liable to be easily crushed immediately after manufacture and before they have had time to harden. If the pitch is too hard it is sometimes modified by admixture with tar oil or creosote. Apart from this the main consideration in the property of pitch is that it should contain little free carbon, the obvious reason being that this acts simply as a diluent. The free carbon content of low temperature pitch is from 5 to 10 per cent. and of high temperature pitches may vary from 15 to 30 per cent. Normally the most satisfactory percentage of pitch varies from 7 to 8 per cent. of the coal. In the case of coke, the percentage is perhaps 1 per cent. higher.

In the manufacture of briquettes the coal is reduced to coarse-powder by disintegration, the pitch being introduced at this stage. If the coal is wet pre-drying is desirable. The crushed mixture, all of which will pass through a ¼-in screen, is passed through a second mixer such as a Pug mill in order to increase intimacy of contact. During mixing the mass is heated by dry or open steam, chiefly the latter, and passes directly to the press. The fusion temperature of the pitch used must be such that melting and spreading is possible at the temperature reached.

Presses may be of several types ; for industrial and power purposes the plunger press forming rectangular briquettes is used, but for special and domestic purposes smaller briquettes are made of prismatic or ovoid shape. Rectangular briquettes have the important advantage that they can be stacked in the minimum of space. The calorific value of briquettes is slightly higher than that of the coal from which they are produced, their specific gravity is approximately 1·2 and the storage capacity of rectangular briquettes is about 50 lb. per cu. ft.

With careful stoking briquettes need not produce more smoke than coal.

The advantages which may be gained by briquetting fuel are not commensurate with the cost of the process, but briquetting forms a means of employing as lump fuel materials which would otherwise be either unsaleable or would command only a low price.

A number of substitutes have been suggested to replace pitch as a binder, the chief reason being the variable price of this commodity. The most important of these are pulp binders produced by the fermentation of vegetable matter, sulphite liquor from the purification of wood cellulose and sea-weed extracts. Briquettes made with pulp binders are weak and are subject to disintegration if wetted. Sulphite liquor briquettes require to be baked after manufacture in order to remove the same tendency to disintegrate on wetting. After baking they are as hard and strong as pitch briquettes. The development of this binder has, however, been retarded by its initial cost and by the limited amount available. Suggestions have also been made for the briquetting of heated coal, making use of the plastic condition of heated coking coal to serve as the binder. This proposal, although sound theoretically, has not met with great success since the temperature to which the coal must be heated causes excessive gas formation and the briquettes break down during cooling.

PULVERIZED COAL AS FUEL

By reduction of coal to a fine state of division and carrying the powder forward into a furnace by an air blast, it is possible to obtain perfect combustion with entire absence of smoke when using the smallest possible excess of air, thereby obtaining high efficiencies of heat transfer. This method of using coal was first introduced to any extent for the firing of rotary cement kilns in which a flame of great intensity and length is desirable. The first successful application was made in 1895 and by 1905 this system of firing had been widely adopted. It was not until considerably later, however, that any appreciable amount of pulverized coal became used for other purposes. The greatest developments took place in the United States in connection with boiler firing for power purposes and a 100-fold increase in the amount of coal consumed occurred between the years 1918 to 1925. In 1925 it was estimated that its use was still increasing at the rate of 200 per cent. per annum. The increases were largely due to developments in steam-raising and to the growth of large central power stations. Advances in this country were slower and did not become of importance until after 1919 when an account by L. C. Harvey of the American work was published by the Fuel Research Board. By 1931 pulverized fuel had been applied widely at collieries, in factories and in central power stations, and during 1934 approximately 1·8 million tons of coal were consumed for steam-raising purposes. In addition 1·5 million tons were consumed in cement and other kilns and perhaps 50,000 tons for metallurgical purposes. It is interesting to note that most of the pulverized fuel installations on land are in conjunction with water-tube boilers, whereas the application to ships is with one exception confined to horizontal boilers. The large combustion space of a water-tube boiler theoretically allows of a much longer flame and of more complete combustion of the coal particles.

The advantages of pulverized fuel systems of firing are similar to those of oil and gas firing and are:

1. Greater flexibility of control is possible and banking and stand-by losses are reduced to a minimum.

2. A wide variety of fuels can be used from coal of low volatile matter in large combustion spaces to high volatile bituminous coals. Low-grade fuels of high ash content can be used provided special precautions are taken to handle the clinker and ash formed and to avoid the carrying of fine dust into the atmosphere.

3. Combustion is complete with a low percentage of excess air; this with high flame temperatures means high thermal efficiency. In large power stations efficiencies of over 90 per cent. have been realized.

4. Maximum fuel economy can be ensured by close regulation of the rate of feed, etc.

5. Labour charges are low and certain repairs can be effected to stokers without waiting for cooling.

6. For metallurgical purposes high flame temperatures are possible and the character of the flame, whether oxidizing or reducing, is under easy control.

Pulverized fuel has also a number of disadvantages, the chief of which has been the relatively high cost of grinding the coal to the necessary degree of fineness. Others are the tendency for slagging of refractory walls and furnace linings, the excessive discharge of fine dust into the atmosphere and the necessity for large combustion spaces to complete the combustion of the coal and avoid deposition of carbon among boiler tubes or in flues. All these disabilities are being gradually overcome by research.

The maintenance costs of a 1929 boiler plant have been quoted by Bruce (*Proc. Inst. Elec. Engs.*, 1932, 71, 541) as 19·6*d.* per ton of coal, the biggest item being 9·3*d.* for repairs to mills, exhauster, etc. In a later plant he quotes only 4·2*d.* for maintenance costs for mills, exhauster, etc., a very considerable reduction. The Institution of Mining Engineers have published data from a number of power stations and have deduced a minimum for running costs of 5·2*d.* per ton and for total costs of 7*d.* per ton. It is, however, unlikely that so low a cost will be assured for some time, even in up-to-date installations.

Suitable Fuels. Practically any dry fuel, whether high or low in ash content or volatile matter, can be burned successfully in pulverized form, but, so far as the coal itself is concerned the most suitable contains over 20 per cent. of volatile matter and is of not more than medium coking power. As the volatile matter in the coal decreases below 20 per cent. the coal becomes rather more difficult to burn completely; low-volatile coals require large combustion spaces if incomplete combustion is to be avoided.

Opinions vary as to the degree of fineness to which coal must be ground, but for satisfactory combustion it is generally accepted that

85 per cent. of the coal should pass a 240 B.S.I. sieve and that none of the oversize should remain on a 72 B.S.I. sieve. When coal is reduced to this degree of fineness it means that a large proportion of the particles are very much smaller than those upper specified limits. The size of a 240-mesh particle is approximately 63 μ (1 $\mu = \frac{1}{1000}$ m.m.) and in coal pulverized so that 85 per cent. passes a 240-sieve it has been shown that 20 per cent. is less in size than 10 μ. The distribution of the different sizes is much the same for all types of coal. Similarly, the shape of the particles does not vary greatly; from air-swept mills they are of irregular shape and have rounded edges, and from other mills they are of similar shape but have sharp edges. Although the above specification as regards size is a general one for all types of coal, it is also true that the correct size for efficient combustion will depend upon the nature of the coal, i.e. coal of low volatile matter should have low particle size, and upon practical considerations such as the size of the combustion space and the behaviour of the coal ash. Where the combustion space is large excessively fine grinding is unnecessary.

Pulverized coal installations may be divided generally into two classes (1) the unit system and (2) the storage system.

The unit system is that in which each furnace has a separate plant for pulverizing and supplying the coal to the burner. The unit system is based upon simplicity of construction and low first cost and is being used widely in recent installations, especially in the smaller type of industrial plant. The unit system consists essentially of a pulverizer placed near the boiler and under the coal feed hopper and driven by a shaft which also drives the fan. The coal is dried in the mill by means of heated primary air drawn by means of the fan through the hollow walls of the furnace This heated air carries the finely divided coal from the mill to the burner, leaving the coarser coal behind for further grinding. At the burner the secondary air required for combustion is supplied at openings round the burner and/or into the combustion space. The amount of primary air must be strictly limited since too much air would make ignition of the air-borne coal difficult. A suitable proportion is 25 per cent. of the total air required for combustion.

The unit system has a number of advantages over the storage system; the most important are, lower first cost, simplicity of construction and saving of space owing to the absence of drying plant, storage hoppers and feeders, and less fire risk. Drying plant may, however, sometimes be necessary with coal of high moisture content.

Up to the present the mill favoured for the unit system has been of the high-speed beater type or the ring roll type, but ball mills of various types are coming into favour, probably on account of low maintenance cost and greater reliability.

A typical unit system is illustrated in the diagram (Figure 7).

The storage system (bin and feeder) was used exclusively in Power Station work until recently. Now, however, owing to interavailability of unit burners this system is also applied. An installation of the storage type includes a crusher, a dryer, pulverizers, storage bins, apparatus for conveying the coal to the furnace and feeders or burners. A diagrammatic arrangement which is typical of such an installation is shown in Figure 8. The coal is first crushed to $\frac{3}{4}$-inch size and passed over a magnetic separator to remove accidental inclusions of metal. The coal then passes to the dryer and to the mill. The powdered coal is air-borne to a cyclone separator placed in a convenient position and conveyed to a hopper from which it is taken in the primary-air stream to the burner.

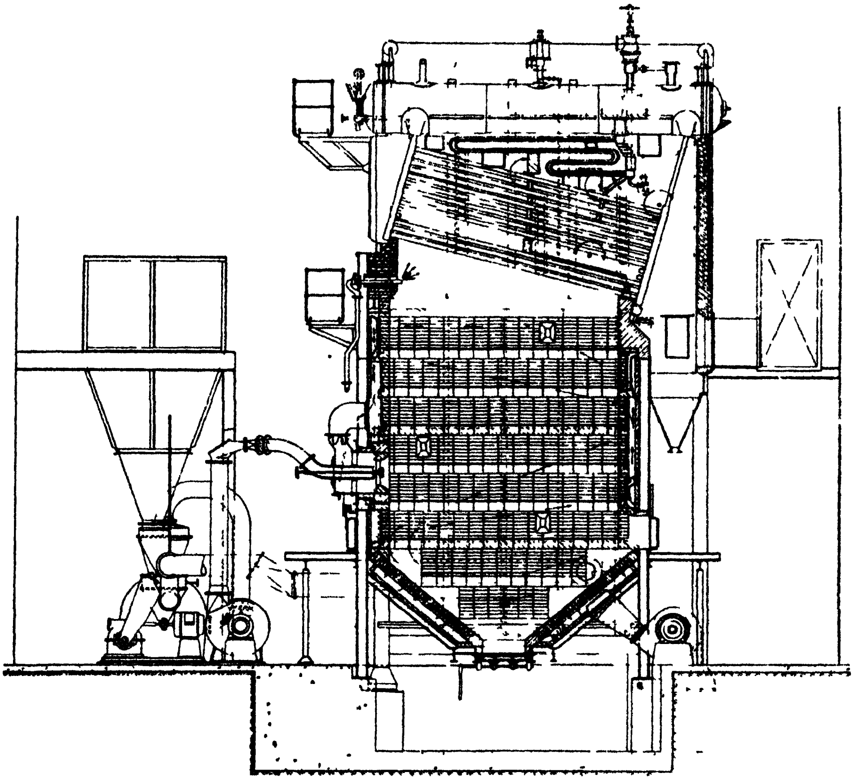


FIG. 7.—Fuller-Bonnot Unit Pulverizer on a Babcock and Wilcox Boiler.

Preparation of the Fuel. In the early days of pulverized fuel firing practically all the coal was dried before grinding. It is now realized that it is only necessary to drive off the surface moisture and that inherent moisture does not greatly reduce the efficiency or capacity of pulverizers. Kreisinger and Blizard (U.S. Bureau Mines, Tech. Paper 316) have shown that coal containing 7 to 8 per cent. of " inherent " moisture can be burned as completely as dry coal. Coal driers may be of several types : (1) rotary driers fired by hot gases, (2) cell-type driers using hot flue gases, and (3) steam-heated. Drying by means of hot flue gas or air is steadily becoming universal. For large systems the coal is dried before grinding ; in the unit system it is dried in the mill by heated air or flue gas.

For the grinding of the coal there are many types of plant available. For large plants the air-swept ball mill is becoming the most popular, and for unit plants the most common are the impact or ring and roller types. The pulverizer shown in Figure 7 is one of the former type; it is shown in detail in Figure 9. The coal enters via the hopper A and is carried forward into the ball mill C shown in partial section. The pulverized coal is carried with the air stream entering at B to the separator D where the larger particles are deposited and return to the mill. Any heavy particles of impurities are removed at E.

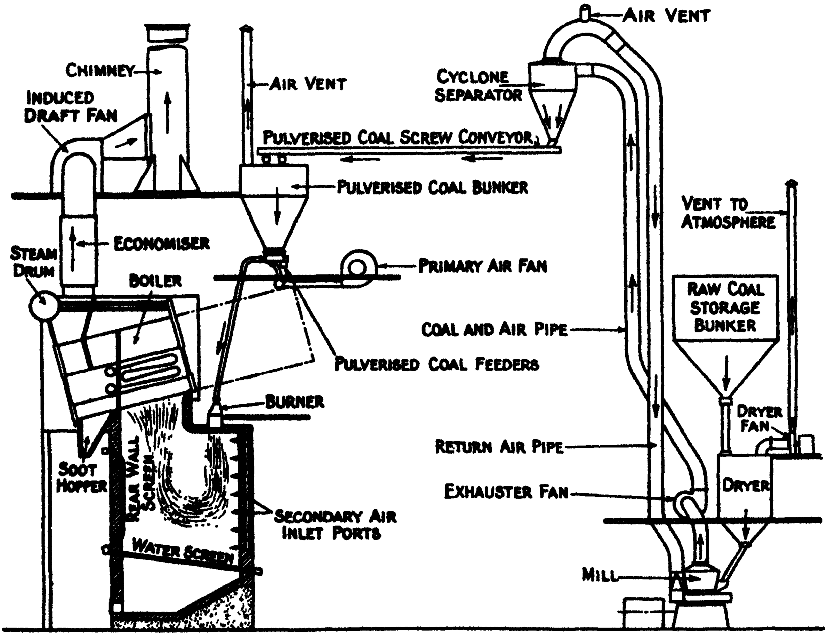


Fig. 8.—Typical Bin and Feeder System.

The air supplied to the mill may be heated to effect partial drying. Generally speaking, the unit system is taken to cost about two-thirds of the larger system per unit of coal pulverized.

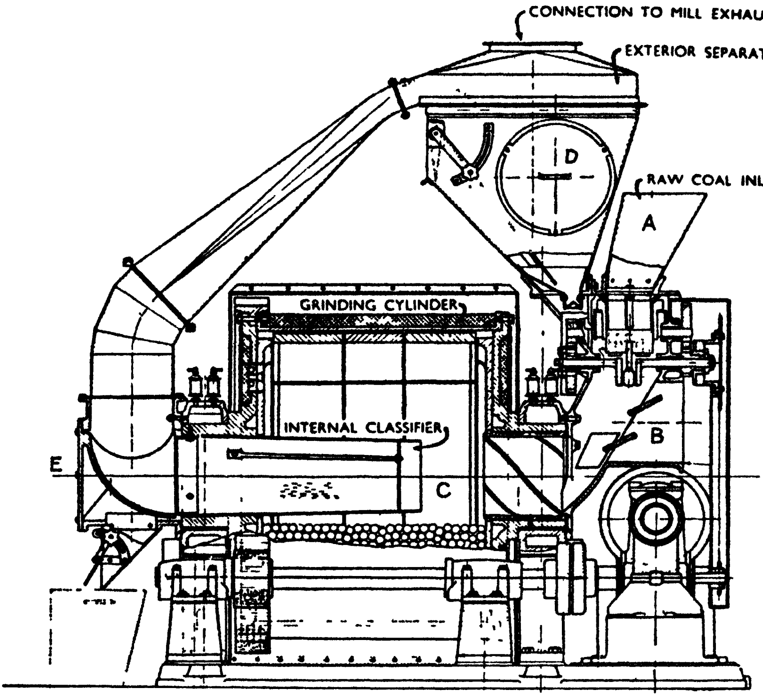


Fig. 9.—Fuller-Bonnot Unit Pulverizer.

Storage. Care must be taken in the storage of pulverized fuel since the dust is liable to spontaneous combustion. For this reason storage for longer periods than eight hours was, at one time, avoided. With better arrangements for enclosing coal storage bins this is now unnecessary and, in the event of firing, the system can be closed and the fire smothered. The only damage done is the caking of part of the coal; this must be removed before the plant is restarted.

Storage hoppers have normally steep sides (not more than 30° to the vertical) in order to prevent the coal arching, and are fitted with air supplies so that the coal can be aerated when necessary to make it flow readily. Storage capacity can be calculated in terms of 60 cu. ft. per ton of coal in the aerated state at about 35 cu. ft. when "packed."

Transportation. Freshly pulverized coal, fluffed with air, behaves as a fluid and its conveyance through pipes is easy. Screw conveyors were originally used, but these have now given way to (1) air suspension, (2) compressed air, and (3) forced aeration systems. Screw conveyor systems were not suitable for distributing the coal over a wide area. In air-suspension systems the coal is carried in a stream of air. The amount of air necessary may be small, only about 400 cu. ft. per ton of coal, or about 1 per cent. of that required for combustion of the coal, or alternatively the whole of the primary air may be used to carry the coal. The arrangement shown in Figure 7 belongs to this system ; the pulverizer coal is aerated in the exhauster and the coal and air transferred to a cyclone separator above the storage bin. The separated air returns to the pulverizer. The system is simple and is in common use where the distance of transport is small. Its main disadvantage is the extra piping necessary for the return air.

The compressed-air system has been fairly widely used. The powdered coal collects in a tank below the pulverizer from which it is blown by compressed air to a bin at the point of use ; the carrying air is separated in a cyclone separator and escapes from an air-vent in the bin cover. Blowing tanks can conveniently be weighed in order to allow of the measurement of coal consumption. The air pressure used is about 50 lb.. per sq. in. and small pipes of 3–4 inches diameter with normal bends can be used. The maintenance cost and power consumption of this system are low.

In the forced aeration system the powdered coal is fed from the weighing tank by a small amount of air into a motor-driven worm pump. As it leaves the pump, air is injected through jets to render the coal fluid and easily transported. The amount of air used is small (about 350 cu. ft. per ton) and narrow pipes can be used to transport coal over long distances. It has been stated that coal has been carried successfully in a 5-inch pipe for a distance of over 6000 ft.

Variations of these systems may be used but the general principles are the same.

Coal Burners and Combustion Chambers. Pulverized fuel burners conform to two main types. The first type may be termed " straight-shot " ; the coal is carried direct into the combustion chamber with from 10 to 25 per cent. of the air required for combustion (primary air). Secondary air, about 25 per cent., is also introduced at the burner and the tertiary air (about 60 per cent.) is introduced through ports in the wall of the furnace. No attempt is made to induce turbulence so that the coal burns with a long flame. With such burners large combustion spaces are necessary to allow of a long path for the flame in which to ensure complete combustion of the coal. Figure 10 illustrates two burners, (*a*) and (*b*), of this type. Figure 8 has already shown one burner in position in a boiler furnace.

In the second type of burner the air is introduced in such a manner as to give as much turbulence as possible and thereby increase the rate of combustion of the coal and reduce the length of the flame. The intimacy of contact between the coal and the air is obtained normally by imparting some form of swirling motion to the air. Figure 10 (*c*), (*d*), illustrates two burners of this type. In the case of the Lodi

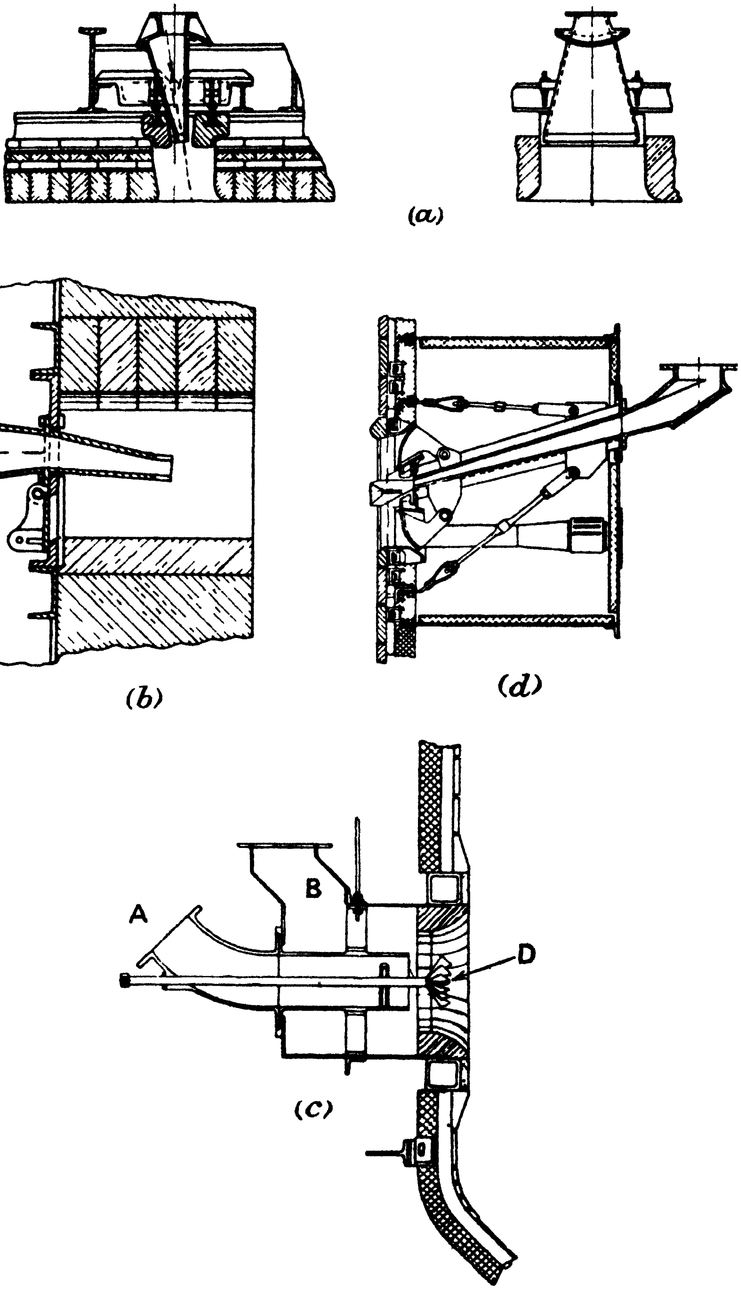


FIG. 10.—Pulverized Fuel Burners.

(a) Vertical, Flare Type.
(b) Horizontal, Flare Type
(c) Short-flame Burner (Lodi).
(d) Short-flame Burner (Cross Tube).
(Messrs. Babcock & Wilcox, Ltd.)

burner, (*c*), the swirling motion is created by the shape of the air ports and the distributor D facing the coal stream.

Coal and primary air (40 per cent. of that required for complete combustion) enter at A. Secondary air enters the box B which surrounds the fuel supply and enters the combustion chamber through specially shaped ports which impart turbulent motion to it. The position of the distributor D affects the nature of the flame ; the nearer it is to the burner, the shorter and more dispersed is the flame.

The Cross-tube burner is shown in Figure 10 (*d*) attached to a water-cooled wall and with adjustable secondary air supplies fed from an air chest round the burner.

Burners of the latter type are being more generally favoured. One important consideration is the reduction which becomes possible in the size of the combustion chamber. The comparative thermal outputs possible in the two cases are 10,000 to 15,000, and 30,000 B.Th.U. per cu. ft. of combustion space respectively.

A modern development of the turbulent type of burner is one in which the required intimacy of contact between coal and air is achieved by stream-lining streams of the coal/primary air mixture with the secondary air. The Grid and Multijet burners are examples of this type. In the former, Figure 11, the primary air carries the coal through a series of long narrow openings formed by the walls of the secondary air ducts and are in the shape of convergent-divergent nozzles. The nozzles accelerate the primary air to a speed which prevents " flashing-back " and then decelerate it to a velocity which allows of easy ignition. The shape of the openings also gives the minimum loss of pressure head. The secondary air is supplied to an annular chamber and thence to the ducts ; it has a considerable cooling effect upon the front plate. Tertiary air is supplied through convenient ports round the flame. With this burner the length of flame is not more than about 6 ft., and very satisfactory results have been obtained even in the limited combustion space of a Lancashire boiler (T. F. Hurley, Fuel Research Tech. Paper 36, 1933).

A modification of the Grid burner is known as the Multijet, in which even greater distribution of the secondary air is achieved by dividing the burner into 49 square nozzles. The coal/primary air streams are in this case surrounded on four sides with secondary air.

In all furnaces it has now become common practice, particularly with large boiler plant, to have cooled walls to encourage the deposition of the fine ash and to protect the furnace linings from severe slagging. These walls may be of diverse types from air-cooled hollow walls to water-cooled pipes and to specially built sections in which the water pipes are encased in cast-iron blocks and reinforced by brickwork. The well-known Bailey wall conforms to this latter type. In the United States the slagging type of furnace is more popular than in Great Britain. In this furnace the flame is directed downwards at an angle upon the surface of a slag well which is insulated so as to retain its heat. The flame keeps the slag molten and the melted mass tends to trap at this point a higher proportion of the dust than do water-cooled walls. The molten slag is tapped off at suitable intervals of time.

With the straight-shot type of burner it is possible to burn from 0·8 to 1·3 lb. of pulverized coal per cu. ft. of furnace space; this is equivalent to a "heat release" of 10,000 to 15,000 B.Th.U. per cu. ft. per hour. With the turbulent type of burner the rate can be increased to about 30,000 B.Th.U. per hour. Greater rates of heat release are to be desired since they give greater efficiencies.

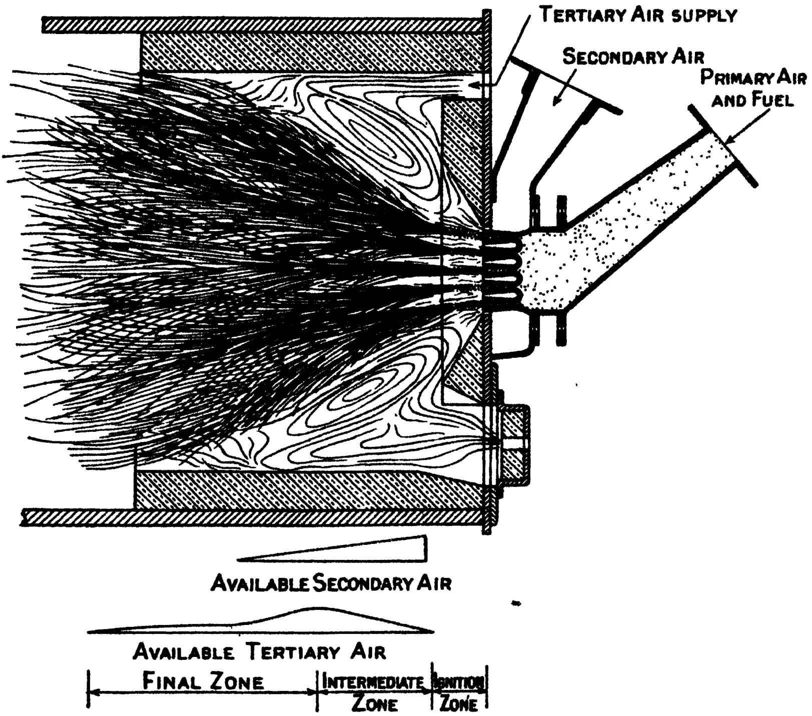


FIG. 11.—Fuel Research Grid Burner arranged for a Lancashire Boiler.

The use of pulverized fuel firing now implies the provision of special means for the removal of the fine dust from the flue gases before these are discharged into the atmosphere. The most successful means are special forms of cyclone separator situated at the base of the chimney. The efficiency of these separators may be as high as 85–90 per cent. Space does not permit of description of these and the reader is recommended to read the papers by K. Toensfeldt (*Fuels and Steam Power,* Sept.–Dec., 1928) and J. W. Gibson (*Colliery Guardian*, 1930, **140**, 234; *Trans. Inst. Min. E.*, 1930, **79**, 45). These methods are being applied to all large boiler plants, whether heated by grate firing or by pulverized fuel.

REMOVAL OF DUST AND OXIDES OF SULPHUR FROM FLUE GASES

The question of dust removal has become complicated by the desirability for the removal also of oxides of sulphur from the flue gases, particularly for power stations situated in populous areas. The first large installation of the kind is applied to stoker firing at Battersea Power Station in London. The washing plant is at present (1934) dealing with the flue gas from seven boilers (out of nine constituting one-half of the boiler-house), consuming 133 tons of coal an hour. The coal is selected to have a low sulphur content—0·8 to 1·0 per cent.; the gas-washing plant will deal with 700,000 cu. ft. of gas per minute, reckoning that it contains 13 per cent. of carbon dioxide, per hour (on completion the station will be generating one and a half million cubic feet, measured at N.T.P., per minute), with a sulphur dioxide content of from 0·02 to 0·05 per cent. Induced draught fans deliver the gas through grit arresters into "primary" chambers, in which it is in contact with steel channels, and then, still in contact with steel channels, through a main flue running the whole length of the building to the chimney at each end. During its progress the gas is continuously sprayed with water, and in this process and in the channels through which it passes, conditions are such that there is a minimum of back pressure. The steel channels and their fillings furnish iron, which, undergoing corrosion and offering iron in the ferric state, effect the oxidation of the sulphur dioxide to the more readily soluble sulphate derivatives, being itself reduced, but re-oxidized by the excess air, so that its action is catalytic. The washing takes place on the counterflow principle. The gas passes to a final scrubber of wood—inert material, wet with an "alkaline solution" of 0·25 per cent. of chalk slurry, and then through a wooden moisture eliminator at the base of each stack, where hot air is added. The "time of contact" of the gas, that is, its time of passage through the system, reckoning the washers empty and the gas at N.T.P., is from thirty to thirty-five seconds. Not less than 90, and up to 95, per cent. of the sulphurous gas is removed from the flue gas, involving a consumption of 20 tons of wash-water and 10 to 12 lb. of chalk per ton of coal consumed, at a cost of threepence for pumping and chalk. The wash water is drawn from, and returns to, the river. During the washing, and in the effluent stage, the water is constantly briskly agitated so that it entrains small air bubbles, which promote the oxidation of sulphites. The reducing power of the effluent is equivalent to three grains of sulphur per gallon, but this can be improved upon by the addition of a small amount of manganese in solution. After filtration, the wash-water is diluted with 25 times its bulk of return condensing water, which is also drawn from the river, and which is alkaline enough to neutralize the acidity that remains after it has mingled with the "alkaline solution" from the final scrubber.

COAL-OIL SUSPENSIONS

During the War it was proposed by Lindon W. Bates that a mixture of pulverized coal and fuel oil should be prepared for boiler firing in order to burn coal under the advantageous conditions of oil firing. It was claimed that the so-called "colloidal fuel" had advantages over both coal and oil, over coal in ease of firing and over oil in having more heat units per cubic foot. To take an example, twenty-six samples of fuel oil from widely distributed sources had a mean calorific value of 19,200 B.Th.U., and with a sp. gr. 0·94, the B.Th.U. per cu. ft. are 1,124,350. With an air dry coal of sp. gr. 1·35 and 14,000 B.Th.U. the B.Th.U. per cu. ft. are 1,177,450. In this country about 2 million tons of fuel oil are used in ships' bunkers, so that replacement by "colloidal" fuel would increase the yearly consumption of coal by 800,000 tons, using a 40/60 coal/oil mixture.

The mixture of coal and oil does not really constitute a true colloid and a more correct term would be coal-oil suspension. Such suspensions are prepared by mixing pulverized coal with fuel oil up to equal proportions. It is a thick viscous fluid which can be pumped only with some difficulty. It is essential that the coal suspension should be sufficiently stable that no deposition of coal takes place in a reasonable time. This can be achieved:

(1) By creating a gel structure in the oil by the addition of a stabilizing agent such as petroleum soap (Greenstreet patent) or lime-resin soap (Lindon Bates) or an alkali salt of a fatty acid.

(2) By using an oil which has the property of high viscosity at low rates of shear. This property is shown by many viscous oils but particularly by cracked residues.

(3) By dispersing or peptizing the coal with a suitable agent such as creosote so that it imparts to the mixture the property of high viscosity at low rates of shear.

(4) By aerating the suspension, as in the Wyndham process.

It is apparent that stability in the first system is infinite provided the strength of the gel is greater than the force exerted by the weight of the coal particle. This is easily achieved since Manning ("Stability of Suspensions of Coal in Oil," World's Petroleum Congress, 1933) has shown that a solution of 0·1 per cent. of sodium stearate in oil will hold up coal particles much larger than those of pulverized fuel. In the other systems stability is not permanent and settling must take place. This can, however; be made slow enough for all practical purposes, i.e. no appreciable deposition in the cold in three months.

In all systems the coal/oil mixture must be intimately mixed by means of a colloid mill or similar machine. It is also desirable in systems 2 and 3 that the coal should contain no particles which will not pass a 240 B.S.I. sieve.

The history of this fuel is interesting. Plauson (*J.S.C.I.*, 1920, **39**, 589A) made the first known suspension in 1913 by means of his well-known mill. During Lindon Bates' experiments sea trials were carried out by the U.S. Scout *Gem* in 1918 on a 30/70 coal/oil mixture containing 1 per cent. of lime-resin soap stabilizer. Land trials were also made at Brooklyn using fuels stabilized with coal tar. During 1922 experiments by the Great Central Railway were reported (Robinson, Modern Transport, June, 1922). A variety of fuels containing up to 60 per cent. of coal were tried in a locomotive with satisfactory results.

In 1932 the S.S. *Scythia* of the Cunard Co. voyaged from Liverpool to New York using on one boiler (4 furnaces) 150 tons of a 40/60 mixture of coal and oil. The burners had to be cleaned about twice as often as with fuel oil, but otherwise there were no difficulties. The oil used was a cracked residue and gave perfect stability during five and a half months.

These experiments show that technically coal/oil mixtures of sufficient stability can be made and burned. Against the 4–5 per cent. advantage which coal/oil mixtures may possess in calorific value per unit volume, must be set the cost of grinding, mixing and stabilizing the product. Troubles in pumping cannot altogether be overlooked. Further experience in practice is required before judgment is possible on the economic aspects of the method.

CHAPTER VII

COKES AND COKING. SPECIAL FORMS OF COKE

COKE

For many generations charcoal was a fuel of great industrial importance and the only one used for the production of iron, for which it is particularly suitable by reason of its high calorific intensity and great purity. As the supplies were becoming depleted, restrictive legislation on its production was imposed, and it became necessary to find some efficient substitute. A fuel low in volatile matter and with a rapid rate of combustion is essential for the high calorific intensity required, and this is best furnished by coke, the porosity of which ensures sufficiently rapid burning; anthracite, low as it is in volatile matter and yet of good calorific value, fails by reason of its density. Consequent upon the introduction of coke with its high resistance to crushing in the furnace and its good combustion with a hot blast at high pressure, it was possible to increase greatly the size and output of the blast furnace.

By submitting bituminous coal to a temperature of over 1000° C. it loses practically the whole of its volatile constituents which include part of the sulphur and nitrogen which escape as gases and vapours, leaving behind a more or less hard cellular mass of coke. The hard, dense but cellular coke essential for metallurgical operations is yielded only by certain classes of coal, in which a perfect fusion takes place; owing to the escape of hydrocarbon gases and vapours a cellular structure is developed, which becomes fixed and hardened at the final high temperature attained, the finished mass retaining none of the characteristics of the parent coal. Reference already has been made (p. 47) to the probable nature of the constituents of coal on which coking is dependent and to the composition of coking coals. When coals contain less of these constituents, as they approach the semi-bituminous coals on the one hand and lignitous coals on the other, the coke pieces retain more or less the original shape of the coal masses, and the material lacks strength.

Whilst the coke produced may for practical purposes be regarded as carbon together with the mineral matter of the coal, it is always found that hydrogen, oxygen and nitrogen are present, and it is possible to obtain gases—carbon dioxide, carbon monoxide but principally hydrogen—from it on further heating in a vacuum. Coke, like all forms of carbon, possesses considerable absorptive power for gases and vapours, which accounts for the presence of some of these gases, and, in addition, some of the complex hydrocarbon bodies are extremely resistant to high temperatures. A well-carbonized coke should not yield more than 1 per cent. of volatile matter (other than moisture) on submitting to strong ignition in a powdered condition.

The escape of the volatile constituents necessarily leads to concentration of the mineral matter of the coal in the coke. Since a high ash is detrimental, the selection of a coal originally low in ash, or the reduction of the mineral matter by suitable picking and washing, is highly essential, and these processes have the further advantage of reducing the sulphur content of the charged coal by eliminating pyrites (see Preparation of Coal, Chapter VI). During the process of carbonization a large proportion of the organic sulphur is driven off, together with some of the pyritic sulphur, and on quenching the hot coke there is a further escape of sulphur by oxidation of ferrous sulphide. It is frequently assumed that the percentage of sulphur in the coke is equal to that in the parent coal but this is only broadly true. During carbonization pyrites (FeS_2) is reduced to iron sulphide (FeS) with elimination of hydrogen sulphide; organic sulphur is decomposed also, giving hydrogen sulphide, and sulphates are reduced to sulphides.

Powell (*Ind. Eng. Chem.*, 1920, **12**, 1009) gives the following distribution of sulphur in coal and in coke quenched out of contact with air:

Form of S.	Coal.	Coke.
Organic	1·79	1·81
Pyritic	1·75	Nil
Sulphate	0·71	Nil
Sulphide	Nil	0·84

In this case the coke yield was about 65 per cent, so that it contained 53 per cent. of the sulphur of the coal. A more average figure is 60 to 70 per cent., and the following may be quoted from coke-oven practice.

	Per cent.
In coke	72·5
In tar	1·5
In liquor	1·7
In gas	24·3

The distribution of nitrogen among the products is also of importance in view of the possible recovery of ammonia. The following data are given by Short (*J.S.C.I.*, 1907, 585):

Observer	Foster.	Knublauch.	McLeod.	Short.
Nitrogen in coke	48·68	50·0	58·3	43·31
„ tar	35·26	30·0	3·9	2·98
„ gas			19·5	37·12
As ammonia compounds . .	14·50	12–14	17·1	15·16
As cyanogen compounds . .	1·56	2·0	1·2	1·43

Owing to the advances in the synthetic production of ammonia recovery from carbonizing systems is not at present profitable.

The calorific value of the combustible part of coke will be practically that of pure coke carbon—8137 calories (14,645 B.Th.U.). King and Williams give 8060 and 8000 cals. for gas and oven cokes respectively, so that the calorific value of a thoroughly carbonized dry coke will be given by

$$\frac{8060 \text{ or } 8000 \times (100 - \text{ash})}{100}$$

The value of coke, however, is more dependent upon the temperature attainable on combustion. This will depend principally upon the coke being sufficiently dense to enable a large number of heat units to be available in a small space; on its being sufficiently porous for rapid combustion, i.e. on its offering a large surface; on the resistance of the surface not actually undergoing proper combustion to the action of carbon dioxide, leading to the formation of carbon monoxide, the action absorbing heat. The presence of excess moisture will necessarily decrease the calorific intensity greatly. Increase of the air blast will intensify the effect up to a certain point for a given coke; beyond this the large excess of nitrogen will lead to cooling, and similarly the use of a hot blast also increases the temperature reached, since more air can be blown through without chilling.

Properties of Coke.

Two main types of coke are produced in industry, metallurgical or foundry coke and gas-retort coke. For both purposes a coking coal is required, but for the latter the most suitable coals are those containing a high percentage of volatile matter since the production of town's gas is the main object of the process. The relative amounts of coal normally used in Great Britain for coke and gas manufacture are 20 and 17 million tons respectively per annum.

The most important properties in coke of all types are strength, freedom from ash, uniformity of size, absence of small pieces (breeze) and high density. In gas cokes which are sold most for domestic purposes the important properties are uniformity of size, freedom from ash and moisture and a reasonable combustibility.

Hardness and Strength. Hardness in metallurgical coke is necessary to prevent undue production of breeze on handling or by crushing under burden in the blast furnace.

The test most commonly used for measuring the strength of coke is the shatter test (Mott, *Fuel*, 1930, **9**, 151). In this test 5lb. of lump coke over 2 inches in size is dropped four times from a height of 6 feet on to a steel plate and the amount of breakage is measured by screening the coke. The following are typical figures for metallurgical and other cokes :

	Gas-retort coke.	Metallurgical coke.			Low temperature coke.
lb. per cu. ft.	30–40	45–55			22
		South Wales.	Yorkshire.	Derby.	
Shatter Test:					
Over 2 in.	76	87·5	78	57	73
„ 1½ in.	88	95	88	72	76
„ 1 in.	95	98	95	88	83
„ ½ in.	98	99	98	97	86
Through ½ in.	2	1	2	3	14

A good gas or metallurgical coke should show 75 per cent. over 2 in., 85 per cent. over 1½ in., and less than 3 per cent. below ½ in. size.

Another test is the tumbler test, in which the coke is rotated in a steel drum for a period and the reduction of size measured.

The hardness of coke is increased by the use of suitable coals or blends, high temperatures and exposure to heat for extended periods. A suitable coal is one which forms a hard coke with just sufficient swelling in the oven to avoid both shrinkage cracks and sticking.

Density and Porosity. In a blast furnace it is essential to maintain an atmosphere rich in carbon monoxide in the reduction zone, and a high temperature in the smelting zone. The latter is assured by the combustion of carbon to carbon dioxide, the former by the action of carbon dioxide on further masses of red-hot carbon, according to the equation :

$$CO_2 + C = 2CO$$

The attainment of these conditions will be dependent largely on the porosity of the fuel and the resistance or otherwise of the cell walls to gaseous action. A highly porous fuel, such as wood charcoal, gives a high calorific intensity, burning practically at twice the rate of coke, but hot wood charcoal is converted into carbon monoxide by the dioxide at approximately twelve times the rate of coke. The relative porosity of the wood charcoal and coke may be taken as 2·6 to 1. High porosity and ease of attack by carbon dioxide would mean large losses of fuel in the upper portions of a furnace. High density means least liability to formation of carbon monoxide, and providing the blast is sufficient to ensure the requisite rapid burning to carbon dioxide, such dense coke will be the most efficient for foundry purposes, where it is obviously desirable to burn the maximum of carbon to the dioxide. In former days high porosity of the coke was essential to the formation of the necessary carbon monoxide by the secondary reaction of carbon dioxide on carbon in the blast furnace, and beehive coke with its hard cell walls, and frequently a ratio of cell space to cell wall of 1 to 1, was an ideal fuel. Under modern blast furnace conditions all coke is sufficiently porous to burn well, and the general tendency is in favour of denser cokes. Weill shows that a diminution of 20 per cent. in the volume of coke means an effective increase of 10 per cent. in the capacity of the furnace, when the volume of coke is assumed to equal half the volume of the charge.

Mott and Wheeler (*Coke for Blast Furnaces*) state that a well-developed porous structure with interconnected open pores is desirable in a blast-furnace coke.

The real specific gravity of coke is that of the carbonaceous elements together with that of the ash, and varies between 1·8 and 2·0. It is the specific gravity of the coke substance exclusive of the pores. The apparent specific gravity is the ratio of the whole coke, inclusive of pores, to that of an equal volume of water. This value lies between 0·75 and 0·95 and, in special cokes, to 1·0. The percentage porosity or volume occupied by the pores is found from:

$$\frac{(\text{real specific gravity} - \text{apparent sp. gr.}) \times 100}{\text{real specific gravity}}.$$

For the determination of the real specific gravity all air has to be removed and replaced by water. If this is attempted in the unbroken material, water-tight cells will obviously lead to considerable error. The total porosity varies from 36 to 60 per cent. An additional value is sometimes obtained for apparent porosity, i.e. the percentage volume of open pores ; a common value is 80 per cent.

So far as hardness of coke is concerned, a compromise is best between dense coke, which may be brittle, and porous coke, which may be soft. If the coke is strong enough the highest temperatures on combustion are achieved with a high percentage porosity, about 55 per cent.

Ash. Not only is high ash detrimental from the point of view of reduction of calorific value and possible influence on metal smelted, but its presence involves expenditure of additional flux in order that it may be removed properly as slag, and also entails an extra consumption of carbon to provide the necessary heat for fusion for this slag. A figure of 2 per cent. of coke for each 1 per cent. of ash is usually accepted. Gill (*J. Iron and Steel Inst.*, 1927, **116**, 91) has shown that 1 per cent. less ash means a saving of 0·4 cwt. per ton of pig iron or at least 4*d*.

Water. The amount present will be dependent primarily on the method of quenching ; 4 to 5 per cent. is common, but in good Durham coke it seldom exceeds 1·5 to 2 per cent. Its presence entails expenditure of heat in evaporation. Mott and Wheeler estimate the consumption for a furnace to be increased or diminished by about 1·2 per cent. for every 1 per cent. of water. Weill, on the assumption that 1 lb. of water requires for its evaporation 0·2 lb. of carbon, estimates that each per cent. additional water entails an increased expenditure of 0·35 ton of coke, and this, together with the charges for water at coke prices, lowers the value per ton by 0·35 fr. (3*d.*) for each one per cent.

Sulphur. The extent of removal of this element during carbonization and quenching has been referred to already, and the effect of sulphur in promoting the formation of hard white brittle iron is well known. The extent to which iron takes up sulphur from the fuel is not definitely known, and much depends upon working conditions. Under the best conditions it should be combined with lime as calcium sulphide and sulphate ($4CaO + 4S = 3CaS + CaSO_4$), and pass off in the slag ; but the slag will retain only a certain amount, largely dependent upon its other constituents. If this amount is exceeded, a greater proportion of fluxing material per ton of pig must be used. Assuming 1 per cent. as the normal sulphur in coke, Weill estimates that to convert this sulphur in 150 tons to calcium sulphide 3·3 tons of limestone are required, and for fusion and expulsion of carbon dioxide a consumption of 1·1 tons of coke. An additional 0·5 per cent. of sulphur is estimated to reduce the value of the coke 0·12 fr. per ton.

Most good cokes contain less than 1 per cent. sulphur. English cokes give a range from 0·75 to 1·3 per cent.

Phosphorus. The importance of this element in coke is great, since it is generally agreed that the bulk of the phosphorus finds its way into the iron. For pig irons to be used for fine castings phosphorus is not detrimental, but in general its bad effects on iron and more particularly steel are well known. According to Weill, Durham cokes contain about 0·012 per cent. ; South Wales, 0·022 to 0·05 per cent. In Pennsylvanian coke the average is 0·01 per cent.

Alkali Chlorides. Alkali chlorides are particularly corrosive to furnace linings, although of no influence on the character of the iron. For this reason coke quenched with brine water may produce serious damage.

Reactivity : Many methods have been proposed for measuring the activity of coke in such chemical reactions as oxidation with air, steam or carbon dioxide, terms such as combustibility and reactivity being used without any precise definition of their meaning. The Fuel Research Division have investigated reactivity towards carbon dioxide and have evolved a standard method for the determination of reactivity

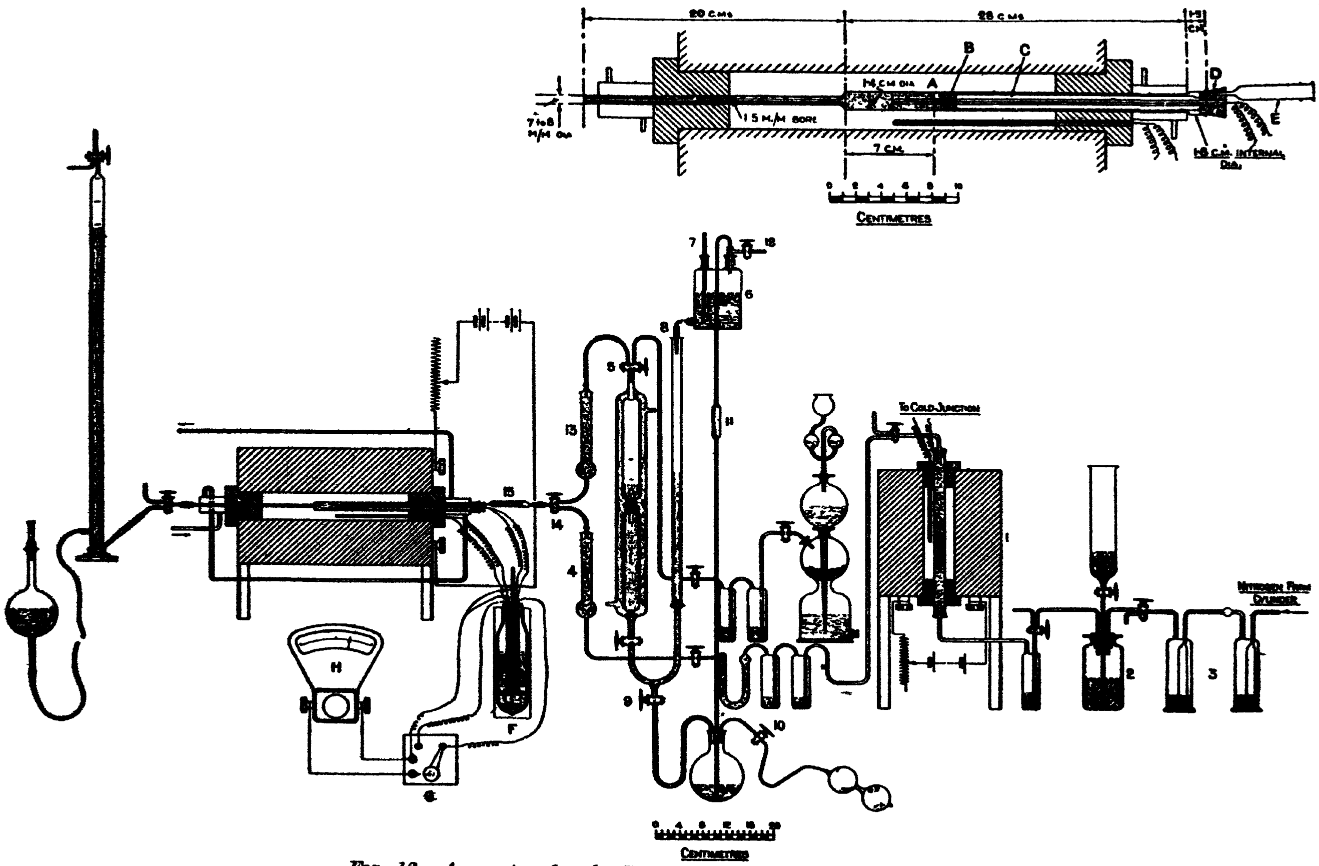


FIG. 12.—Apparatus for the Determination of the Reactivity of Coke.

values. The method involves the passage of CO_2 over heated coke under standardized conditions and the measurement of the carbon monoxide formed. The chosen temperature, 950° C., is such that the equilibrium mixture of the system C, CO, CO_2 corresponds to 98·7 per cent. CO. 100 ml. of CO_2 under these conditions would give 197·4 ml. of CO as the limiting value for reactivity. The apparatus is shown in Figure 12.

The reaction tube, of clear silica, is shown in detail in the smaller drawing and contains a constant volume (7 ml.) of coke graded 10–20 I.M.M. The silica tube may be connected to (*a*) a stream of pure nitrogen or (*b*) a stream of pure carbon dioxide. The nitrogen is purified by the system 1, 2, 3, Figure 12, 1 being reduced copper heated to 600° C. The carbon dioxide is generated in the Kipps apparatus, washed and passed to the gasholder 5, from which it is expelled by a concentrated solution of magnesium chloride 6. Each section of the gasholder has a capacity of 100 ml. On leaving the holder the gas is dried by phosphorous pentoxide 12 and 15 and enters the reaction tube at E. In a determination nitrogen is used to sweep the apparatus, then 100 ml. of CO_2 are passed through and the products allowed to escape, followed by 100 ml. of CO_2, the reaction product being measured in the nitrometer.

The reaction temperature used is 950° C.

In this method, three reactivity values have been identified. Reactivity I is the number of ml. of carbon monoxide formed from 100 ml. of carbon dioxide under conditions which give as closely as possible the initial reactivity value. The value for reactivity falls off with continued heating, and Reactivity II is an apparently constant value which is reached after complete removal of volatile matter from the coke. Reactivity III. is a lower constant value reached by continued action of carbon dioxide on the coke. Characteristic curves are shown in Figure 13 for certain industrial cokes, and the values taken from the curves are shown in Table XXVI.

TABLE XXVI

REACTIVITY VALUES OF INDUSTRIAL COKES

	Reactivity value.		
	I.	II.	III
Maximum	197·4	—	—
1. Charcoal, beech	180	—	160
2. Gas-retort coke	120	72	59
3. By-product oven coke	98	72	57
4. S. Wales metallurgical coke	73	67	42
5. Beehive coke	43	40	42

It has been shown that the reactivity value is greatly affected by the presence of easily reducible iron compounds. The Reactivity I value is that at which the ash exerts its full effect, the iron being in the metallic state, while R. III represents the value when the iron is present as ferrous oxide and almost inactive, i.e. the R. III value represents a close approximation to the ash-free reactivity of the coke. Metallurgical cokes contain very little reducible iron and therefore give flat reactivity curves. In cokes containing a high amount of reducible iron, as for example the vertical retort coke giving the curve shown in Figure 13 (0·2 per cent.), an approximation to the R. III can be obtained without prolonged passage of carbon dioxide either by extracting the soluble iron with mineral acids or by adding to the coke the requisite amounts of hydrogen sulphide, silica, alumina or titania to combine with the iron and render it inert.

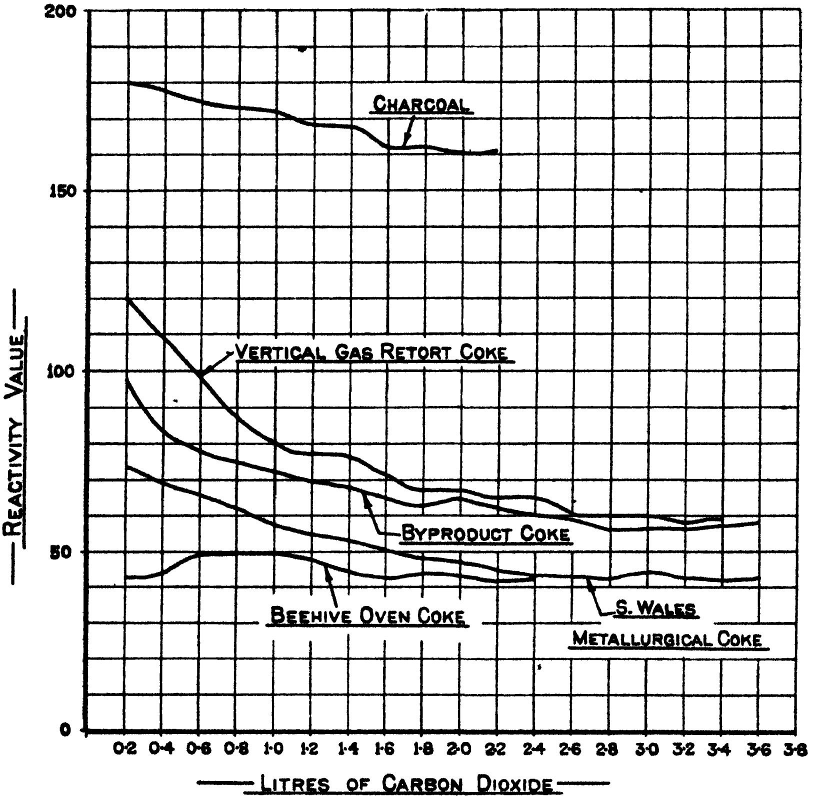


Fig. 13.—*Reactivity Curves of Typical Cokes.*

The precise importance of reactivity values in industrial processes has not been defined. In blast furnace practice a high solution loss is associated with reactive cokes and possibly a lower rate of reaction at the tuyères with non-reactive cokes. Where two effects such as these are operative it would seem that the problem would be solved by using a coke which would give a low solution loss but which after oxidation by the tuyères would become reactive and increase its activity in that zone.

In water-gas practice the same double effect operates. High reactivity is an advantage for the water-gas reaction itself but a disadvantage during the blow reactions. In producer gas practice the reactive coke is obviously the best.

For metallurgical purposes Mott and Wheeler (*Coke for Blast Furnaces*, 1930) prefer to measure combustibility by a method based upon those of Haüsser and Bestehorn and the U.S. Bureau of Mines. They use a fuel bed [1–1½ in. coke] of 14 in. depth in a laboratory furnace of 1 sq. ft. area and, under controlled conditions of air blast, determine the composition of the gases at a series of 8 points in the fuel bed at 1½ in. intervals from the grate. Temperatures are also read opposite these points by means of an optical pyrometer. The results are expressed as "reactivity with oxygen" of the coke expressed as the distance above the grate at which oxygen is no longer present in the gases; "reactivity with carbon dioxide" as the distance at which the gases contain 20 per cent. or more carbon monoxide; and the maximum temperature of the fuel bed. In the corresponding U.S. Bureau of Mines method, Sherman and Blizard (*Trans. Amer. Inst. Min. Eng.*, 1923, **69**, 526) compare reactivities by the ratios $\frac{CO_2 + CO}{2CO_2 + CO + 2O_2}$ Comparative values for beehive coke, by-product oven coke and charcoal were 72, 67 and 95 respectively.

Certain selected values from Mott and Wheeler's work are as follows:

TABLE XXVII

Reactivities of Metallurgical Cokes

Type of coke.	Oxygen disappears at in.	20 per cent. CO at in.	Max. temp. of fuel bed. °C.
Charcoal	3	5	1560
Beehive	6	>12	1800
Blend of coking and non-coking coal .	4	7	1685
Yorkshire coking coal . . .	4	11	1700

Cokes of high reactivity with oxygen are produced from non-coking coals or by blending coking coals with weakly-coking materials. Cokes made from strongly-coking coals alone have low values. Reactivity values with carbon dioxide generally follow the same order. The maximum temperatures developed follow only in a general sense since this depends also on other properties, such as porosity.

So far as blast furnace conditions are concerned, it is concluded by Mott and Wheeler that a satisfactory hearth temperature is most economically maintained with a reactive coke *containing but little* breeze, and that the size and hardness of coke are factors of greater importance than specific reactivity.

Production of Coke. In the manufacture of metallurgical coke the object is to attain the highest possible yield of serviceable coke from a given coal, i.e. to fix as much of the carbon of the coal as possible in the coke, regarding gas and tar as by-products. Coke is also obtained in coal-gas manufacture, but in this case it is a by-product, the primary object of the gas-maker being to obtain as much of the carbon as possible in the gas in the form of hydrocarbons of high calorific power.

The earliest methods of obtaining coke were similar to those in vogue for charcoal burning, the restricted combustion of the coal in piles or in stacks with brick flues, this partial combustion furnishing sufficient heat to carbonize the remainder; but such wasteful methods are practically obsolete. The natural development was combustion of the volatile constituents in a dome-shaped oven, arranged for suitable and easily-regulated air admission, above the surface of the coal, so that the heat slowly penetrated downwards and effectually coked the mass. These beehive ovens are still employed to the extent of about 10 per cent. in Great Britain for the manufacture of particularly refractory coke for special purposes.

The beehive ovens are from 12 to 13 ft. in diameter, 7 ft. high; the coal is charged to a depth of about 3 ft. To economize heat the ovens are built in two rows, back to back, with a common flue arranged down the centre, the waste heat passing off under boilers.

For successful results in such ovens the coal must have good coking properties, as the temperature at which coking commences is low, and the rise of temperature not rapid, since the previous charge has been cooled in the oven by water, and the oven has usually been standing two or three hours before recharging.

The slow initial rate of heating promotes the formation of well-developed cell structure, and the final high temperature attained ensures a dense hard character to the product. Low temperatures lead to irregularity in coking, lack of coherence and inflated cell development.

The natural development to avoid the loss of coke substance was the introduction of ovens from which the combustion products could distil through suitable orifices in the walls, and meet the air necessary for combustion only in an exterior space. By the use of long horizontal rectangular ovens, closed by doors at the ends (Coppée), the coal could be charged conveniently and the coke pushed out by mechanical means; or in vertical ovens with a slight taper (Appolt) the coke could be dropped when the lower doors were opened. With the beehive ovens or ovens of the above pattern far more gas was utilized for heating than necessary, and although the waste heat was to some extent recovered by passing the gases through boilers, the losses were great, and further all the valuable by-products were lost.

The average yield of a retort oven as compared with a beehive oven working on the same coal will be approximately 10 per cent. higher.

The modern oven consists of long rectangular chambers, 30 to 35 ft. long, 9 to 14 ft. high, and 14 to 22 in. wide, closed by doors at either end, so that charging is performed at one end, the coke being pushed out by suitable discharging machinery and quenched at the other end. A section through a Becker oven is shown in Figure 14, the coke being in process of discharge. A number of ovens are built up side by side to form a battery, the bottoms being heated by combustion of the gas in sole flues, and the sides by a suitable arrangement of flues between adjacent ovens. The main differences between the numerous forms of coking plant are to be found in the arrangement of the flues in order to secure the most effective and uniform heating; on this the success of the operation is entirely dependent.

The discussion of these various forms of construction is outside the scope of this volume; in the earlier forms the side flues were horizontal, the hot gases passing from end to end two or three times (Simon-Carvés, Semet-Solvay, Hüssner, etc.); but now these are not so favourably regarded, preference being given to vertical flues (Coppée, Otto-Hoffmann, Otto-Hilgenstock, Koppers, new Simon-Carvés, Collin, etc.), since it is more easy to obtain uniform heating.

Modern recovery plants are constructed for working on the "waste heat" or "regenerative" principle. In the waste heat type the hot gaseous products of combustion pass through boilers where they meet any surplus gas, which undergoes combustion, so that steam is raised for works purposes. The temperature of the flue gases is from 920° C. to 1100° C. (1700–1950° F.), and with water-tube boilers 2 lb. of steam have been raised from and at 212° F. per lb. of coal carbonized; with Lancashire and similar boilers from 1 to 1·25 lb. can be obtained.

In the regenerative system continuous or alternate methods are employed; with the first, the hot gases pass through suitable firebrick channels to the chimney, and the air for combustion passes in the reverse direction through parallel channels, and so becomes heated. In the alternate method, the arrangement is similar to that of Siemens, at least two chequers of firebrick being used; during the heating up of the one the other is imparting its heat to the incoming air, necessitating reversals at frequent intervals, so that the oven flues are at times acting as heating flues, and at others as exhaust flues. If the sections affected by the reversals are large, this leads to considerable trouble with brickwork through its alternate expansions and contractions, and the heating is never uniform. All modern improvements aim at the multiplication of

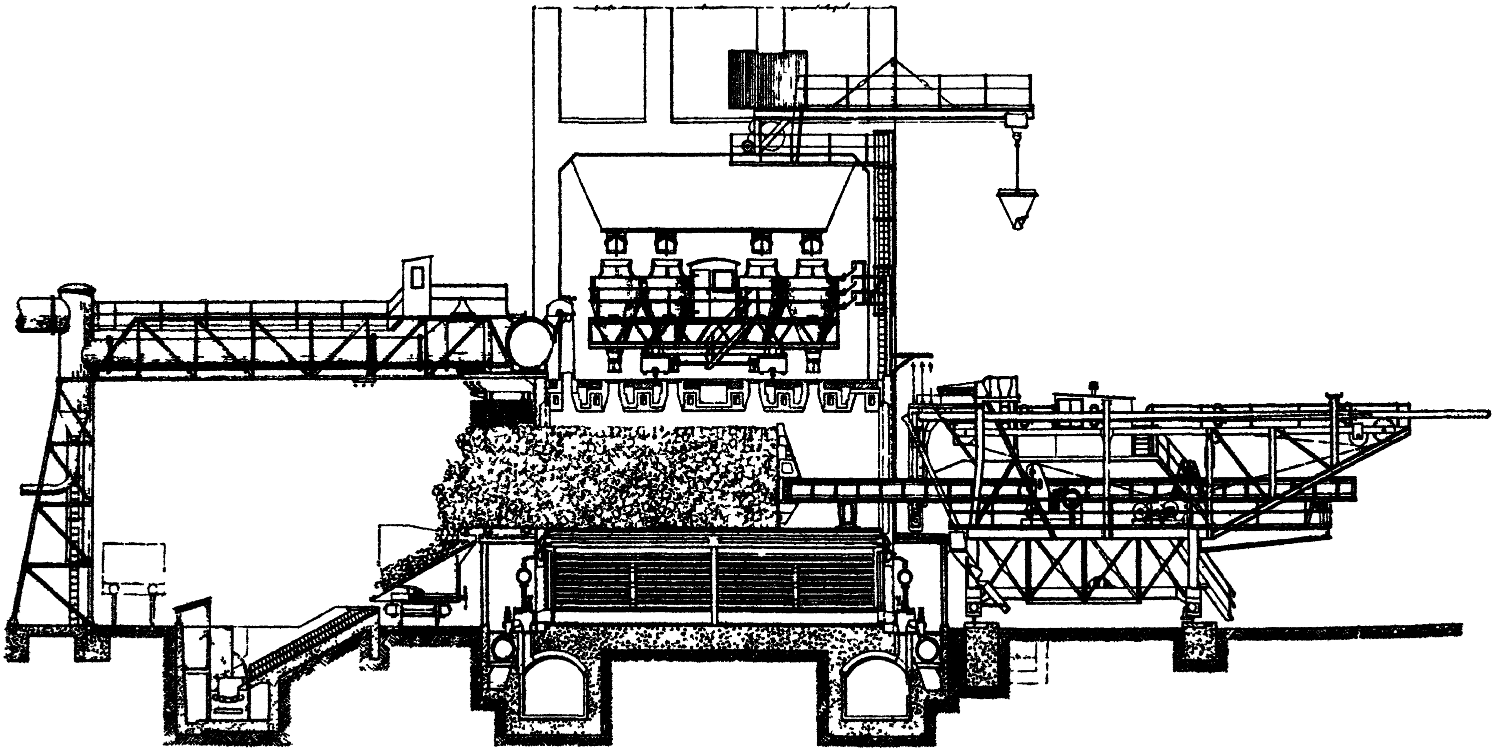


FIG. 14.—Section through a Becker Coke-Oven, showing the Discharge of the Coke.

(The Woodall Duckham Vertical Retort & Oven Construction Company (1920) *Ltd.*

the number of sections ; in the most recent ovens reversals are confined to alternative vertical flues.

The temperatures employed are as high as possible, up to 1400° C. in the combustion chambers, and to allow of this the ovens are constructed of silica brick (96 per cent. SiO_2).

With regeneration only a portion of the distillation gases are required for heating the ovens, so that there is considerable surplus gas which is available for power purposes or for sale. Naturally this surplus entirely depends upon the character of the coal, but with most coking coals it exceeds 50 per cent. Much of this gas is available for sale and this, together with the composition of the coke-oven gas, is fully dealt with under Gaseous Fuel (p. 263), and estimates of the quantity which may become available for use on p. 140.

The distinctive arrangement of the three types non-recovery plant and recovery plant with waste heat and with regeneration will be made clear by the diagrammatic plan shown in Figures 15, 16, 17.

In coking the best results are obtained with coal of small size ; in modern practice large coals are crushed to pass through a ¼-in. screen (60 per cent. below ⅛ in.). This procedure is important in that it allows of the utilization of slacks provided they are clean. In some plants the coal is compressed in a stamper and charged into the oven in a solid mass slightly smaller than the inner dimensions of the ovens. From 10 to 12 per cent. of moisture is usual in the crushed coal, and this ensures sufficient binding for the mass to retain its proper shape when the retaining walls of the compressor are let down. The moisture also prevents the loss of fine coal dust in the gases evolved, which takes place with dry fine coal. By compression a charge some 25 per cent. heavier can be got into each oven, and the coke produced is firmer and more dense. In other ovens the coal is charged from the top.

The charges and time of carbonization vary greatly with the type of oven and to some extent with the nature of the coal. Beehive ovens take 10 tons, the period of carbonization being about seventy-two to ninety-six hours.

By-product ovens vary in coking time with the width of the oven. A 14-in. oven takes 11 hours and an 18-in. oven 16 hours and their throughputs are 30·5 and 28 tons of coal per day. Modern practice favours the 16 to 18-in. oven as giving the best compromise between strength, rate of heating, size of coke and output.

Influence of Conditions on the Coke. The suitability of modern recovery plant coke and its efficiency as compared with beehive coke is no longer questioned. The poorer results with earlier retort cokes were due probably to an insufficient temperature being attained, with consequent lack of hardness in the cell walls.

The influences which are of importance in the manufacture of coke are (1) the nature of the coal, (2) its size, (3) its moisture content, (4) the method of charging, (5) the rate of heating and (6) the method of quenching.

In general, the type of coal should be such that it has sufficient

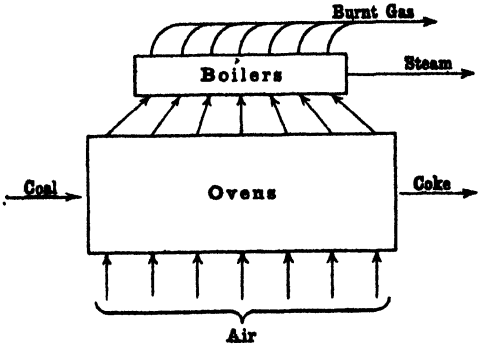


Fig. 15.—Coke-oven plant, non-recovery of by-products.

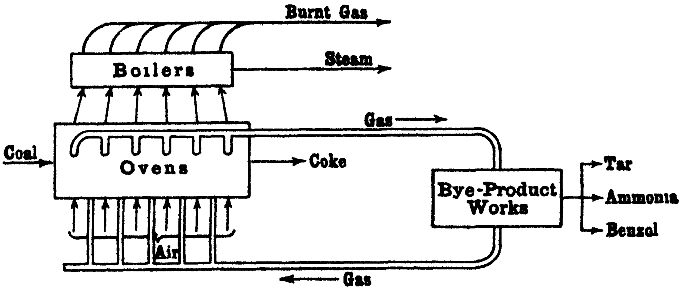


Fig. 16.—Coke-oven plant, by-product recovery, waste heat type.

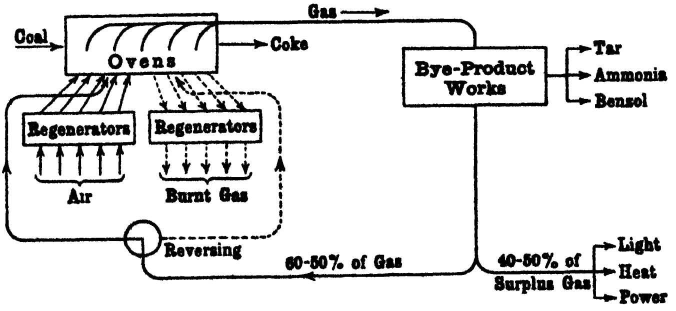


Fig. 17.—Coke-oven plant, by-product recovery, regenerative type.

coking and swelling power to give on carbonization a well-developed porous structure which is retained during the hardening which follows. The very fusible coking coals which were necessary for the beehive oven have too high a coking power for the modern patent oven and tend to give a frothy and porous coke which is weak through excessive shrinkage and the formation of cracks. The blending of coals for coking purposes is now widely adopted, the high coking power of the former coking coals being modified by admixture with coals of poorer coking power, anthracite, coke dust, etc., to give charging stocks which have the correct properties for the type of oven to be used. Blending also serves as a means of modifying such properties in the coke as reactivity, density, hardness and porosity. One very interesting blend constituent is fusain dust, and it is indicated that an optimum quantity of 3 per cent. added to coking coal gives large coke of increased hardness. Finely crushed coke is a good substitute for fusain. The most satisfactory size for coking coal is such that the coal contains no pieces larger than ¼ in. and that over 60 per cent. passes a ⅛-in. screen. Finer grinding has no material advantage, the important point being exclusion of any coal larger than ¼ in.

It is generally accepted that the most satisfactory amount of moisture in coking coal is about 5 per cent. This fact is important in view of the increasing use of washed slacks. Too dry coals appear to give more fissured coke, whereas too wet coals require more heating and longer periods of carbonization. Mott and Wheeler indicate a decrease of coking time from thirty-six to twenty-six and a half hours for a reduction of moisture content from 13·0 to 1·0 per cent.

There are two methods of charging ovens, top-charging of the loose coal and side charging of blocked coal. In general, top-charged cokes are less fissured, stronger and of better size.

Rate of heating is probably the most important consideration in coking. In narrow ovens the rate of heating would be too great for highly-coking coals and blending is essential. If this is adopted the best results seem to be obtained at rates of coking of from 0·85 to 0·95 in. per hour. Narrow-oven coke, the result of a high rate of heating, has been found to be superior to wide-oven coke for blast furnace purposes. The superiority appears to lie in hardness, uniformity made possible by blending and more even heating, and closer grading of size.

Quenching of oven coke is done by water spraying in a coke car or on an inclined bench, and is done so carefully that the finished coke should contain less than 1 per cent. of moisture. The coke car gives the most uniform result. Dry quenching by the circulation of inert gases has been adopted to a slight extent in America and in gas manufacture.

Recovery of By-products. Three systems are employed for the recovery of the by-products. The oldest of these, the Indirect system, is exactly similar to that in the gas industry—condensation of the tar and ammonia liquor, extraction of the last traces of the tar by some form of tar extractor, followed by water-washing to extract ammonia from the cooled gases. For gas engine use, favoured in a few collieries, the gases are passed through a filter followed by iron oxide purifiers to remove H_2S. This system is becoming increasingly popular again because for economic reasons, as will be shown later, it is sometimes desired not to recover ammonia. The gasworks system, known as the Indirect system, is the only one that does not involve recovery of some portion of the ammonia.

The Indirect system is uneconomical from a fuel consumption standpoint, and produces a large bulk of effluent which cannot be discharged into rivers, and involves difficulty in its disposal. The Direct and Semi-Direct systems both aim at the avoidance of these difficulties. In the Direct system the gases are kept above the dew-point (70 to 80° C.) until after the ammonia has been entirely extracted. The hot gases are treated with a spray of tar under high pressure (Otto system); in a cyclone extractor (Simon-Carvés system), or in an electro-static precipitator to remove the tar fog. After passing through the exhauster, generally of a high-speed turbo-type, the gases containing the whole of the ammonia, with the exception of that portion combined as chloride and sulphate—the "fixed" ammonia—travels direct into a lead-lined vessel known as the saturator in which they are caused to bubble through dilute sulphuric acid, all but the last traces of the ammonia being in this way extracted from the gases. In the Semi-Direct system, the inconvenience of dealing with the very large volume of hot gases containing the whole of the water charged into or generated in the coke oven is avoided, but the fuel consumption of the plant is increased. The gases leaving the oven are cooled to atmospheric temperature, thereby eliminating the tar, and all the water not retained by the gas at a temperature of, say, 25° C. The liquor thus condensed contains the whole of the fixed ammonia and about half the free ammonia and is distilled in special stills, the steam and ammonia gases being passed back into the gas stream just before the saturator.

Wherever benzole is to be recovered the gases must be cooled. This creates no trouble in the Indirect system, it leads to the whole of the water—contaminated with highly-poisonous substances and naphthalene—being deposited in the Direct system, and to some water deposition in the Semi-Direct system. The question of effluent disposal is always acute when benzole is recovered. The cooled gases are washed by creosote oil, by petroleum oil, or are passed through active carbon (Beckton) or through silica gel, to recover the benzole. The benzole absorbed by the liquid or solid agents is recovered therefrom by treatment with steam, and must be further washed and purified to fit it for motor or chemical uses.

Many attempts have been made in the past to utilize the sulphur contained in the gases to furnish the sulphuric acid necessary for the production of sulphate of ammonia. Of historical interest are those of Feld, Burkheiser, and the recent attempt of Koppers and Hansen

(C.A.S. process): all these processes have failed either from technical difficulties or because, as at present, the manufacture of sulphate, even by such processes, is uneconomical.

Further information on modern coking processes may be found in the following books:

International Handbook of the By-Product Coke Industry; W. Glund, E. Benn, Ltd., 1932.

Motor Benzole, W. H. Hoffert and G. Claxton, London, 1931.

Coal Carbonization, Chem. Cat. Co., N.Y., 1924.

Gas Manufacture, A. Meade, Benn Bros., 1921.

Economic Aspects of By-product Recovery. The recovery of by-products in coke manufacture, formerly of the greatest economic importance, has in recent years suffered severely from adverse markets for tar and, particularly, sulphate of ammonia, the markets for the latter being invaded by synthetic ammonia. The result has been a great reduction in manufacture and the problem of disposal of unwanted liquor has become acute.

As an offset to this slump have come better markets and a protective tariff for benzole and improved facilities for the sale of surplus gas. Benzole has improved in production, 49 million gallons of crude being produced in 1933 from 30·4 million tons of coal carbonized.

The sale of gas has been steadily increasing as an adjunct to town gas supplies. In Yorkshire a gas "grid" has been established (*Colliery Engineering*, 1931, p. 284) into which all coke ovens already established in that area can supply gas for subsequent distribution. At a basic price of 5½*d*. per 1000 cu. ft., this sale of gas means a new credit to an efficient coke-oven plant of about 4*s*. per ton of coal carbonized, ranging downwards to something below 2*s*. for an old and inefficient installation. Very little gas has yet been sold from this grid (1933), but it is hoped to find an outlet for some 80,000,000 cu. ft. per day. The problem of disposing economically of coke-oven gas in all districts has not yet been solved, but there are indications that erection of all new coking plants near or even owned by steel works will prove the ultimate solution.

LOW TEMPERATURE CARBONIZATION

In the early days of gas manufacture coal was carbonized in metal retorts at temperatures in the neighbourhood of 800° C. The gas yield was low and the coke produced was relatively combustible. In modern processes of gas manufacture, the temperature is raised to a high level in order to obtain a high yield of gas. This procedure produces unavoidably a coke which is much less reactive and is unsuitable for combustion in domestic appliances in which a strong draught is not available, or in which the heat losses are not reduced to a minimum by insulation with brickwork.

The damage caused by smoke from domestic and factory chimneys created early in the twentieth century interest in the manufacture of smokeless fuels which would mitigate the nuisance. Attention was naturally directed towards the manufacture of the more combustible cokes produced in the early days of gas manufacture, and T. Parker appears to have been the first to demonstrate the practicability of this by carbonizing coals between 500 and 600° C. in iron retorts.

Since then many processes have been tried with varying degrees of success and considerable sums of money have been spent in endeavouring to carry to a successful issue the commercial carbonization of coal on these lines, the advantages of such low-temperature carbonization being:

1. The production of a smokeless fuel suitable for burning in an open grate of the type normally used for coal, and without modification thereof.

2. The production of a high yield of tar of low viscosity, differing from ordinary coal tar and more suited for conversion into liquid fuels, thereby providing a home source of fuel oil.

3. The abatement of the smoke nuisance in cities.

The advantage of replacing a large proportion of the raw coal used for domestic purposes by a smokeless fuel is admitted, and the possibility of obtaining at the same time home supplies of liquid fuel, including motor spirit, adds further to the economic importance of low-temperature distillation. This is not confined to coal suitable for producing smokeless fuel, since much low-grade cannel and similar material can by low-temperature carbonization be made to give high yields of "oils." During the war Government interest was naturally directed to the question of home supplies of liquid fuel, and experimental work was carried on by the Petroleum Executive and by the Ministry of Munitions. Since 1920 the problem has been dealt with by the Fuel Research Division of the Department of Scientific and Industrial Research and details of the progress of the work can be found in the annual reports of the Director of Fuel Research.

The ease of combustion of coke made at temperatures of 500 to 600° C. was first ascribed to its softer nature than gas coke, the absence of graphitization and the presence of some 8 to 12 per cent. of volatile matter in it. These views were modified by reason chiefly of the researches of Sutcliffe and Evans (*J.S.C.I.*, 1922, 196 T.) and Sir G. Beilby (*J.S.C.I.*, 1922, 341 T., and Fuel Res. Board Rept., 1922). These investigators show that if a suitably minute cell structure is determined in the coke it may be of a dense, hard character but yet free burning.

A serious disadvantage of most of the low-temperature coke has been its friability, leading to the excessive production of "breeze" in transport and handling. This has formed a difficulty in most processes and has been overcome in different ways, by better choice of coals, by blending and briquetting.

An important practical difficulty in carrying out low-temperature carbonization has been the transmission of heat through the coal. With externally-heated retorts too high a retort-wall temperature has meant excessive carbonization of the outer portions of the charge by the time the interior has been satisfactorily carbonized. This has enforced low flue temperatures, and consequently a low rate of thermal transmission. To counter this and obtain a reasonable time of carbonization it has been assumed that the coal must be treated in thin layers, or kept in motion in a stream of hot gas, and that the retort material must be a good thermal conductor, i.e. metal. Experience with metal retorts, chiefly cast iron, has not been happy, castings having a very short life if the temperature rose to about 600° C. New cast irons are now showing more promise and this disability may be removed in the future. The Fuel Research Board, after experimenting for a number of years with metal retorts, has changed over to brick retorts of similar design (Fuel Research Tech. Paper, 35, 1933). Although using a higher flue temperature the inner surface temperature is limited to about 600° C. and the combustibility of the coke is not reduced.

The various processes which have been put forward can be classified in terms of the method of heating the coal, as follows: The names of the best-known processes only of each type are quoted:

1. External heating of static charges in thin layers: Parker (coalite), Beilby, Tozer, Hird, Illingworth.
2. External heating of moving thin layers in metal or brick retorts: Beilby, Fuel Research, Crozier.
3. External heating in retorts with mechanical devices for moving or stirring the coal: Fusion, Freeman, Salermo.
4. Internal heating by combustion of part of the coke, i.e. semi-producers giving low-grade gas: Midland Coal Products, MacLaurin, Bussy.
5. Internal heating with superheated steam: Turner.
6. Internal heating with sensible heat of hot gases in rotating cylinders: L. & N., K.S.G., Thyssen.

As is to be expected, the products from such diverse methods of treatment must vary very widely. It would be impossible to discuss the variations here and the reader is directed to a review of the situation in 1928 by Sinnatt (*Fuel*, 1928, 7, 305). One important difference is the type of solid fuel produced: in certain processes, where the solid product from the retort is necessarily of small size briquetting has to be resorted to, to produce a lump fuel. Where the briquettes are made with pitch subsequent stoving is necessary if the fuel is to be smokeless.

The yields of the various products have also varied within wide limits, partly owing to the above differences in system and partly owing to indifferent technique in assessment.

TABLE XXVIII

Yields of Products from Certain Low-Temperature Carbonization Processes

From the results of Tests by the Director of Fuel Research

Name of Retort.	Fuel Research.[1]	Parker (Coalite).	Freeman.	Crozier.	MacLaurin.	Bussy.	L. & N.
Coal	Dalton Main.	Dalton Main.	Kirkby Top Hard.	Tullygarth Hawkhill Seam.	Virgin.	Bothwell.	New Lount.
Yields per ton of dry, ash-free coal:							
Coke, cwt. . .	13·93	14·70	16·75	14·46	11·27	9·96	3·35
Breeze, cwt. .	1·87	0·72		3·04	1·20	2·04	10·70
Gas, cu. ft. .	7,050	6,220	2,150	8,390	34,150	47,890	102,200
Gas, therms .	49·4	43·9	19·3	27·1	79·6	90·3	37·8
Tar, gals. . .	20·1	20·1	22·3	18·6	18·3	20·9	15·7
Spirit, gals. .	—	1·2	—	0·9	0·3	0·1	Nil
Liquor, gals. .	27·6	11·0	11·8	—	49·5	29·1	—
S./ammonia, lb.	10·5	15·0	3·9	10·3	43·1	22·7	—

[1] Fuel Research Tech. Pap. 35, 1933

Table XXVIII gives yields which have been obtained on a variety of plants during tests by the Fuel Research Board. The yields are typical of most of the retorting systems quoted above and can be summarized as follows for bituminous coal systems producing rich gas:

Coke	14–15 cwt.
Tar	18–22 gals.
Motor Spirit from gas . .	1–2 „
Liquor	10–30 „ (incl. cond. steam)
Gas	2000–7000 cu. ft.
„	30–50 therms

Some idea of the progress made in this country can be gained from the fact that over a quarter of a million tons of low-temperature smokeless fuel were sold in this country during 1933. There is no doubt but that each year will see substantial advances.

In certain processes in which the solid product from the retort is finely divided the fuel has an industrial rather than a domestic application unless briquetting is resorted to, to produce a lump fuel.

Low Temperature Carbonization Products. The amount of volatile matter remaining in the solid residue depends upon the method of treatment and the temperature to which the coke has been subjected. It is now accepted that for lump smokeless fuel of the Coalite type 5–8 per cent. is sufficient to impart free-burning properties. Smokeless fuels are normally light, though certain forms and particularly briquettes are fairly dense. Normally the bulk density varies from 18–22 lb. per cu. ft. as compared with 24–28 lb. for gas retort coke, and 50–55 lb. for domestic coal.

FIG. 18.—Apparatus for Measuring Radiation from Fires.

The Fuel Research Board have devised a method of test for smokeless fuels in which a measured volume is burnt in the grate and the component of radiation in one direction measured, the results being compared against a standard in terms of ease of ignition, maximum radiation, time to reach maximum radiation and percentage of fuel consumed. Such tests for domestic fuel are now becoming commonly applied. The general arrangement of the apparatus used is shown in Figures 18 and 19. In the open fire, smokeless fuels are easily ignited and have the high radiation efficiency of over 30 per cent. of the total heat of the fuel, compared with 22 per cent. for coal. In certain grates the absence of long flames is a drawback in the case of oven and water heating, but suitable grates can be constructed.

Tar.—Low-temperature tar is a somewhat variable product owing to the many processes involved, but in general its characteristic properties are rather a function of the temperature than of the type of process. The maximum yield of tar is obtained with a carbonizing temperature of 550–600° C. Generally low-temperature tars have a lower specific gravity than gas tars (1·02–1·06 against 1·10) and are of lower viscosity. They contain little free carbon, 0·2 per cent., and little naphthalene and anthracene ($<$ 1 per cent.) although substitution products of these are present in fair quantity.

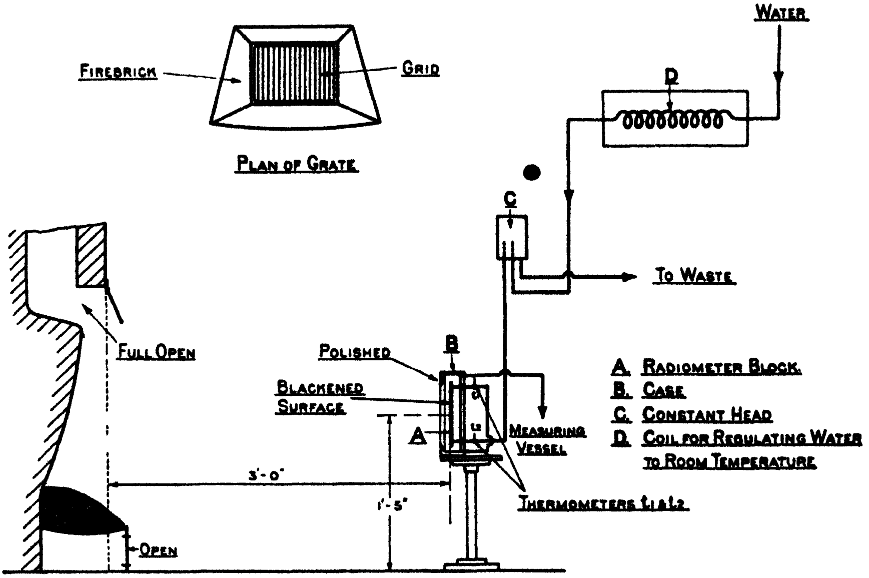


Fig. 19.—Diagram of Apparatus for Measuring Radiation.

Perhaps their most striking feature is their high content of tar acids (up to 35 per cent.). These are normally of higher molecular weight than the tar acids of gas-retort or coke-oven tar, the lowest member, phenol, being present to the extent of only 1 per cent. The greatest production of tar acids corresponds approximately to a carbonizing temperature of 550° C.

Low-temperature tar contains aromatic hydrocarbons, but the proportion is definitely less than in high-temperature carbons. The same hydrocarbons are present, even including benzene (about 0·5 per cent. of the tar) but generally those of low-temperature tar are of higher molecular weight. In addition the tar contains saturated, unsaturated and polymethylene (naphthenic) hydrocarbons. The saturated hydrocarbons amount to less than 6 per cent. and consist to a fair extent of solid paraffins, as much as 2 per cent. being found in one tar.

TABLE XXIX

COMPOSITION OF LOW-TEMPERATURE TARS

Percentages by weight of the dry tar

Process.	Fuel Research.	Illingworth.	Parker.	MacLaurin.	Turner.	Salermo.
Coal	Dalton Main.	Beeston	Mixed.	Scottish.	Ell.	Coventry Beans.
Yield, gals. per ton of coal	20·0	18·0	17·5	19·1	22·1	15·0
Specific gravity . .	1·05	1·08	1·04	1·07	1·02	1·04
Distillation:						
Water	2·0	2·9	3·1	4·9	3·7	5·5
Tar oil . . .	60·5	56·2	64·6	47·8	57·1	65·3
Pitch	39·2	43·7	35·2	52·1	42·7	34·7
Loss	0·3	0·1	0·2	0·1	0·2	0·3
Analysis of Tar-Oil:						
Tar acids . . .	21·0	21·7	23·5	18·1	16·8	25·3
Bases	1·9	1·8	1·3	1·3	2·0	1·3
Neutral oil . .	37·6	32·7	39·8	28·4	38·3	38·7
Total	60·5	56·2	64·6	47·8	57·1	65·1
Tar acids:						
0–210° C. . .	4·1	8·6	6·6	4·1	0·3	4·7
210–220 . . .	3·5	3·0	3·0	1·8	1·8	2·4
220–290 . . .	5·7	4·5	6·1	7·2	7·1	9·0
300–360 . . .	5·6	4·3	5·6	3·9	5·4	6·4
Residue . . .	1·5	1·0	1·9	0·8	2·0	2·4
Loss	0·6	0·3	0·3	0·3	0·2	0·4
Total	21·0	21·7	23·5	18·1	16·8	25·3
Neutral Oil:						
0–170° C. . .	4·1	2·3	6·0	0·8	5·8	2·5
170–230 . . .	7·9	8·2	8·2	4·5	6·8	6·3
230–360 . . .	21·3	19·4	23·5	20·6	24·7	25·2
Residue . . .	3·7	2·4	8·7	2·1	0·7	4·1
Loss	0·6	0·4	0·4	0·4	0·3	0·6
	37·6	32·7	39·8	28·4	38·3	38·7

Morgan has described the properties of the "resinoids" of tar, i.e. those amorphous or resinous constituents of high molecular weight which are insoluble in light petroleum but soluble in many organic solvents. On evaporation from solution they yield the resins as hard transparent films. The resinoids constitute as much as 15 per cent. of the tar and contain mainly neutral (resinene) and phenolic (resinoid) bodies with small quantities of resinamines and resinoic acids.

The approximate composition of a number of typical tars are shown in Table XXIX.

Further details of the constitution and properties of low-temperature tars and oils can be found in the following publications:

Sinnatt and King, *J.S.C.I.*, 1925, **44**, 413 T.

Sinnatt, King and Linnell, *J.S.C.I.*, 1926, **45**, 385 T.

Tars and Oils from Coal. Fuel Research Technical Paper No. 32, 1931.

Morgan, *J.S.C.I.*, 1932, **51**, 67 T.

The utilization of low-temperature tars in existing markets has been delayed partly owing to the fact that the products do not fit specifications which have been drawn up primarily for high-temperature tar products. This difficulty is gradually disappearing and low-temperature tars and fractions are certain to find their own market when sufficiently large supplies are available; it has been stated for example that the pitch produced is particularly suitable for briquetting purposes. Low-temperature tar is also suitable for direct conversion into motor spirit and Diesel oil by catalytic hydrogenation (see page 176).

Gas.—The gas produced by external heating at about 600° C. differs widely from town gas in that it contains a much higher proportion of hydrocarbons and less hydrogen. It has a higher calorific value and a high density. It can be used for heating the retorts, but its most obvious outlet would be for enriching coal gas for towns' purposes. The gas from certain processes such as the MacLaurin, where internal heating is used, is of low calorific value owing to dilution of the rich gas with producer gas.

The compositions of three gases are shown below in comparison with a town's gas.

	Fuel Research.	Parker.	MacLaurin.	Town gas. Greenwich.
CO_2	4·0	4·0	9·5	1·7
C_nH_m	3·4	4·3	0·9	3·1
CO	6·7	6·2	14·0	7·4
H_2	31·8	37·6	26·2	51·2
C_nH_{2n+2}	43·5	40·0	8·1	29·2
N_2	10·6	7·9	41·3	7·4
"*n*"	1·27	1·25	1·27	—
B.Th.U. per cu. ft.	725	710	233	560
Sp. gr. (air = 1)	0·65	0·56	0·74	0·40

When stripped, low-temperature gas yields about 1·5 gallons of motor spirit per ton of coal. Although this type of spirit is high in unsaturated hydrocarbons (up to 35 per cent.) it is easily refined by washing with sulphuric acid and caustic soda, and forms, after mixing with the spirit obtained by distilling the tar, a motor spirit of high anti-knock value (see page 220).

PART II

LIQUID FUELS

CHAPTER VIII

COMPOSITION, PRODUCTION AND CHARACTER OF FUEL OILS

Until recent years it was generally understood that a liquid fuel was a heavy residual oil, either from petroleum or coal tar, capable of being burned either for steam-raising, or for heating operations in metallurgical or other furnaces, but the introduction of internal combustion engines has given the term a much wider significance.

In the earlier days of the petroleum industry, when kerosine was the most important product of the crude oil, a large part of the residue, after the removal of the lower-boiling naphthas and lamp oils, had little outlet but as fuel oils. Further, many of the highly asphaltic oils, with the methods of distillation then practised, were incapable of yielding marketable products other than motor spirits, kerosines and fuel oil residues. The latter constituted an abundant, cheap and very efficient fuel and its use in the refineries, and for locomotives and marine purposes developed rapidly.

The introduction of the internal combustion engine using in the first place the highly volatile gasoline (commonly known as *petrol*) gave a greatly enhanced value to the naphtha fraction, previously of little value.

The development of such engines and their application to the motor-car, the submarine, the dirigible balloon and aeroplane, which have completely revolutionized our ideas of locomotion, and rendered possible that mastery of the sea in submerged craft and the conquest of the air so long sought by man, have been possible only by reason of the suitability of light oils or spirits for such engines, enabling the maximum of heat units to be carried in minimum space and efficiently employed in the engine.

Later there followed the Compression-Ignition ("C.I.") type of engine (familiarly spoken of as Diesel engines) and the hot-bulb engine (often referred to as the semi-Diesel), both of which enabled heavy oils to be used.

In one form of engine or another practically the whole range of distillation products, and in some cases residuals, from petroleum is available as fuel, and so important have fuels for I.C. engines become that suitable ones have been sought in other raw materials, coal tar, and to a limited extent alcohol.

Although a heavy oil from petroleum, or with some limitations from coal tar, may be employed either for external or internal combustion, it is convenient to consider liquid fuels under separate headings —those used for steam-raising and general heating purposes, and those used in internal combustion engines. The former are referred to generally as fuel or bunker oils; the latter as Diesel oils.

Liquid Fuel for Steam-raising. The advantages of liquid fuel for steam-raising as compared with coal are great, and may be summarized as:

High Calorific Value: 1 lb. of oil fuel averages 19,500 B.Th.U. as compared with 13,500 B.Th.U. for good coal. This is due to the inherent high calorific value of the hydrocarbon constituents, and to the high purity of oils, the amount of non-combustible matter usually being almost negligible.

The theoretical evaporative value of petroleum fuel oil is thus about 20 lb. of steam per lb. of fuel; one eminent firm will guarantee 16·5 lb. from and at 212° F. when the rate of evaporation does not exceed 4–5 lb. per square foot of surface, and 14 lb. with evaporation at the rate of 16 lb. per square foot.

Low Stowage Value: 1 ton of oil averages 38 cu. ft. as against an average for coal of 43 cu. ft.

The high calorific value and low stowage value enable a greater number of heat units to be carried or stored per cubic foot of space than for coal in the ratio of 1·7 to 1.

Further, oil can be stored on shore in tanks below the ground level, thus economizing in space, or on board ship stored in fore or aft compartments or the double bottoms, situations impossible for solid fuel, the bunkers for which must be situated conveniently in relation to the stoke-hold.

These properties, in the case of vessels of the mercantile marine, leave valuable space free for cargo; in battleships, they add enormously to the radius of action of the vessel.

Easy Control of Consumption: This being effected by opening or closing the valve, or by putting into or out of action additional burners, is a simple operation, and any desired rate of steam production can readily be ensured; further, a steady steam pressure can be assured.

Economy in Staff: Control being so easy and the heavy labour in coal-trimming and handling abolished, great reductions of stoke-hold staff are possible. This is important in the mercantile marine from the point of view of wages and provisions. In the Navy it means a reduction in the crew, with less loss of life in the event of a vessel being sunk in action, and a greater proportion of the crew available for fighting the ship.

Since the war a considerable number of large liners have been converted to oil fuel firing at great expense. Many new vessels have been equipped to burn oil. This is sufficient evidence of the advantages, practical and economical, of oil fuel.

Cleanliness : Bunkering with coal, especially on board ship, must be always an extremely dirty process, and result in valuable time being spent in cleaning up. Since oil can be pumped through suitable hose directly into the tanks no dirt is distributed. Further, in the case of battleships, the practicability of taking in oil supplies in this manner while under way at sea is an important matter.

Again, oil burns without residue, so that the handling and disposal of ashes, clinker, etc., are obviated. The amount of inert matter in the form of ash carried with coal is often overlooked; 2000 tons of bunker coal with 5 per cent. of ash means shipping no less than 100 tons of useless material. The absence of ash, moreover, leads to better efficiency, as the opening of the doors for cleaning the fires is rendered unnecessary.

Other minor advantages are the non-deterioration of oil in storage, the absence of danger from bunker explosions with oil of satisfactory flash-point, lower stoke-hold temperatures, no corrosion of the bunker plates, and the abolition of the excessive physical exertion in stoking.

The advantages of liquid fuel are not confined to steam-raising; its high intensity of combustion, and the ease with which a steady temperature can be maintained over a long period, and the facility of control are very favourable to its use in many metallurgical and other industrial operations. The heating systems of many large buildings are now operated with liquid fuel, consumption being regulated by thermostatic control. For many purposes the absence of ash and the low sulphur content of most oils are greatly in favour of its employment.

The advantages to be derived from the use of liquid fuel in place of coal are unquestionable, and the matter resolves itself largely into considerations of supplies and price. In the British Dominions generally, and in Great Britain in particular, the bulk of oil suitable for fuel must always be imported, and the continuity of supplies, which has even under peace conditions suffered interruption, with consequent great advance in price, demands careful consideration. The economic aspects of oil fuel are deferred for discussion in a later chapter.

Characteristics Necessary in a Fuel Oil. The oil should have a high calorific value; the highest will be found with those oils consisting almost entirely of pure liquid hydrocarbons. Oils containing any quantity of oxygen compounds, such as tar oils, have necessarily a lower calorific value. For safety in use the oil must not give off inflammable vapour until a temperature well above any likely to be attained in use is reached, that is, its *Flash-Point* must be high. In the mercantile marine the flash-point must not be lower than 150° F. (close test), and for Naval use below 175° F. In order that the oil may flow readily through pipes it must not be too viscous at ordinary temperatures. Many natural oils and residues contain so much solid hydrocarbon in solution that on lowering the temperature they become semi-solid. The oil should be as free from water as possible, or there is a risk of the burners being extinguished, and free from solid matter, otherwise the fine orifices of the burners will become choked.

For domestic heating burners light grades of oil are used, these being distillates.

The quality of fuel oils is specified by the U.S. Bureau of Standards in Fuel Oils, Commercial Standard CS 12–33 (1933). There are six grades of fuel oil listed in this publication.

REQUIREMENTS FOR FUEL OIL 1, 2 AND 3

(All temperatures are degrees F.)

Grade—(see note).	Flashpoint		Water and sediment max. (%)	Pour max. (deg.)	Distillation		Viscosity (max.).
	min. (deg.)	max. (deg.)			10% (deg.)	90% (deg.)	
No. 1 .	110	165	0·05	15	420	(E.P.) 600	—
No. 2 .	125	190	0·05	15	440	620	—
No. 3 .	150	200	0·10	15	460	675	55 Saybolt (100° F.)

Note.—These are distillate oils for use in burners requiring: No. 1, a volatile fuel; No. 2, a moderately volatile fuel; No. 3, a low viscosity oil.

Grade—(see note)	Flashpoint		Water and sediment max. (%)	Pour min. (deg.)	Distillation			Visc. max.
	min. (deg.)	max. (deg.) Above			10% (deg.)	E.P. maximum (deg.)	90% (deg.)	
No. 4 .	150	250	1·0	15	—	—	—	125 Saybolt (100° F.)
No. 5 .	150	—	1·0	—	—	—	—	100 Furol (122° F.)
No. 6 .	150		Water with sedmt. not above 2%	Sedmt. 0·25	—	—	—	300 Furol (122° F.)

Note.—No. 4, low viscosity fuel; No. 5, medium viscosity fuel (Bunker B.) No. 6, high viscosity fuel, (Bunker C).

Sulphur requirements may be specified as follows:

No. 1, 0·5 per cent.; No. 2, 0·5; No. 3, 0·75; No. 4, 1·25; Nos. 5 and 6, no limit.

The most generally used oil in the United States for "domestic" burners is No. 3, whilst heavy oil for furnace purposes is No. 6—Bunker "C."

Small modifications of these requirements have been "recommended" (1934); an additional feature being the introduction of carbon residue figures of 0·05 per cent. for Grades 1 and 2, and 0·10 for Grade 3.

The following is a copy of the specification issued by the British Admiralty:

> 1. *Quality.*—The Oil fuel supplied under this Contract shall consist of Liquid Hydrocarbons, and may be either:
>
> (*a*) Shale Oil; or
>
> (*b*) Petroleum as may be required; or
>
> (*c*) A distillate or a residual product of petroleum; and shall comply with the Admiralty requirements as regards flash-point, fluidity at low temperatures, percentage of sulphur, presence of water, acidity and freedom from impurities.
>
> The *flash-point* shall not be lower than 175° F. close test (Pensky-Martens). [In the case of oils of exceptionally low viscosity such as distillates from shale, the flash point must be not less than 200° F.]
>
> The proportion of *sulphur* contained in the Oil shall not exceed 1·5 per cent.
>
> The Oil fuel supplied shall be as free as possible from *acid*, and in any case the amount of inorganic acidity present must be such that not more than 10 mgm. of potassium hydroxide are necessary to neutralize the acidity of 100 grammes of the Oil.
>
> The quantity of *water* delivered with the Oil shall not exceed 0·5 per cent.
>
> The *viscosity* of the Oil supplied shall not exceed 1000 seconds for an outflow of 50 cubic centimetres at a temperature of 32° F., as determined by the Redwood Standard Viscometer (Admiralty-type for testing Oil fuel, p. 357).
>
> The Oil supplied shall be free from earthy, carbonaceous, or fibrous matter, or other impurities which are likely to choke the burners.

As a result of trials conducted by the Admiralty on low-temperature tar-oil fuels the following specification was drawn up:

Flash point—Pensky-Martens . .	not below 175° F.
Sulphur	not to exceed 1 per cent.
Crude Tar Acids	„ „ „ 36 „
Pitch	„ „ „ 2 „

To be free from inorganic acidity and sensibly free from anthracene and sediment.

Solids separating out after maintaining the oil at a temperature of 32° F. for seven days shall not exceed 0·1 per cent. An important point in connection with tar-oil fuels is the effect of tar acids on the calorific value. On an average this is reduced by about 35 B.Th.U. per lb. per 1 per cent. of tar acids.

The following is a summary of a specification for Creosote for Fuel in Furnaces issued by the British Standards Institution (*No. B.S.S.* 503, 1933):

The creosote shall consist essentially of a distillate of coal tar and shall be free from admixture with petroleum oils and undistilled crude tars.

It shall be free from sediment and other impurities likely to choke burners.

Specific gravity at 38° C. (100° F.) not above 1·07.

Viscosity at 100° F. not above 100 seconds. Redwood No. 1.

It shall become completely liquid on being slowly warmed to 38° C.

On cooling it shall remain free from separated solids. After standing for two hours at 32° C. (90° F.).

Flash-point shall not be below 150° F. Pensky-Martens.

Ash—not above 0·05 per cent.

Gross calorific value—not below 16,000 B.Th.U.

Available Fuel Oils. The available fuel oils are heavier portions of natural petroleums and shale oils, tar oils derived from coal distillation, blast furnace tar, water gas tar, and tar from gas producers.

PETROLEUM

As crude petroleum is the source from which the bulk of oil fuels —ranging from petrol to heavy oil—is obtained, its general characters and distillation may be described conveniently here, the individual distillates being considered more fully later.

Petroleum occurs widely distributed throughout the world, but the two greatest oil-producing regions are those of America and the Russian fields, and the oil-fields of California, Texas, Mexico, Venezuela and Persia have assumed considerable importance. In the East, oil is found in quantity in Burma and the Eastern Archipelago, notably Borneo. The British Empire does not contain any important oil-fields, but there are small outputs of oil in Canada, Australia, New Zealand, Newfoundland, Trinidad, and Barbadoes. Table III (Appendix) shows the world's output in metric tons.

Physical Characters.—The origin of petroleum is still a matter of debate and need not be considered here. As obtained from the borings it varies in colour from a light yellow to almost black; some oils are highly mobile, whilst others are thick and viscid. Redwood found the lowest specific gravity (0·771) in samples from Washington U.S.A., and Sumatra, and the highest (1·06) in a Mexican sample. According to the same authority, the range for American oils is between 0·785 and 0·945, and for Baku oils 0·85 to 0·90.

The *flash-point* may be from below the freezing-point of water up to 320° F.

The *coefficient of expansion* (the ratio of the increase in volume for 1° to the original volume) with rise of temperature is an important property, and due allowance must be made for this in estimating deliveries under different temperature conditions. The lower the specific gravity of the oils, the greater is the rate of expansion. For heavy oils, this is 0·0007 per ° C. (0·00039 per ° F.), and for lighter oils 0·00072–0·00076 per ° C. (0·00040–0·00042 per ° F.). For Roumanian petroleum Petroni gives—

Specific gravity.	Coefficient of expansion per ° C.
0·730 – 0·820	0·0009 – 0·0010
0·830 – 0·870	0·0008 – 0·0009
0·870 – 0·910	0·0007 – 0·0008

The *specific gravity* of oils in Great Britain and the United States is taken at 60° F. relative to water at the same temperature. For an oil temperature differing from 60° F. the standard correction per Fahrenheit degree is as follows:

"Spirits" Below sp. gr. 0·740	0·00048
"Spirits" Above „ 0·740	0·00044
Kerosine	0·00040
Gas oils	0·00036
Diesel engine fuels	0·00035
Heavy fuel oils	0·00034

The *viscosity* of petroleum oils varies greatly even with oils from the same district. It increases with rise of specific gravity, the higher value for both being dependent mainly upon the presence of heavier hydrocarbons, possibly solid paraffins held in solution by the higher liquid paraffins, but no connection can be traced between viscosity and specific gravity, oils of the same specific gravity varying widely in viscosity. Increase of temperature causes a rapid decrease in the viscosity, and a rise of a few degrees will often cause a sluggish oil to flow freely.

The *specific heat* is frequently important, since it is often necessary to heat fuel oils before use. The specific heat decreases almost *pro rata* with a rise in specific gravity. The following are values for crude oils:

	Specific gravity.	Specific heat.
Pennsylvania	0·8095	0·5000
California	0·9600	0·3980
Texas	0·9200	0·4315
Russia	0·9079	0·4355

Determinations made by one of the authors are:

	Specific gravity.	Specific heat.
Russian	0·914	0·448
Burma	0·897	0·433
	0·924	0·406
Texas	0·927	0·436
Shale	0·880	0·460

The calorific value of petroleum and heavy oil fuels is dealt with at the end of the present chapter.

Chemical Composition of Petroleum. Petroleum consists almost entirely of the elements carbon and hydrogen, together with small and varying quantities of oxygen, nitrogen and sulphur. According to Veith, the proportions are:

Carbon	79·5–87·1	average	84·5
Hydrogen	11·5–14·8	„	12·5
Oxygen, etc.	0·1– 6·9	„	2·0

The sulphur in petroleum seldom exceeds 1 per cent., but over 2 per cent. occurs in many Texas oils, and still higher quantities in some Mexican crudes. Average American petroleum contains about 0·5 per cent. Occasionally a small amount of free sulphur is present, but in general the sulphur is present in the form of organic sulphur compounds. To these compounds the objectionable odour of many petroleums and of their first distillation products is due. During distillation some decomposition takes place with production of sulphuretted hydrogen.

High sulphur content was formerly objected to on the grounds of possible corrosion of metals by the products of combustion. This is now regarded as insignificant, except where condensation of water, etc., occurs, but funnel gases and engine exhaust gases are rendered highly objectionable by the presence of much sulphur dioxide.

Hydrocarbons Present in Petroleum. By a combination of chemical treatment and refined methods of fractional distillation a large number of hydrocarbons have been isolated from petroleums, and it has been established that all natural oils consist of mixtures of numerous hydrocarbons belonging to various well-recognized series, and members of at least eight such series have been identified. By a " series " is meant a succession of definite compounds, the individual members, as one ascends in molecular weight, showing a regular difference in the number of carbon and hydrogen atoms present, and it is therefore possible to write a general formula for the members.

Of these eight series of hydrocarbons the following are the principal:

Paraffins	Olefines.	Naphthenes or polymethylenes.	Benzene or aromatic.
C_nH_{2n+2}	C_nH_{2n}	$n(CH_2)$	C_nH_{2n-6}

The lower members of a series are frequently gases, soon passing into easily condensible liquids, and finally through more and more stable liquids until solid substances are reached. Increase in molecular complexity is then accompanied by rise in boiling-point in the case of liquids, or of melting-point in the case of solids, and the rise in these properties is also associated with a rise in specific gravity and viscosity. Thus, in the case of the paraffin hydrocarbons, the first four members are gases; at C_5H_{12} (pentane) is a very volatile liquid; the subsequent liquid members increase in boiling-point and density until about $C_{18}H_{38}$ (octdecane) jelly-like hydrocarbons (mineral jelly or vaseline) are reached, and these finally are succeeded, about $C_{21}H_{44}$, by solids, which in various mixtures constitute paraffin wax.

The character of a natural oil and the proportion of different commercial constituents (petrol, illuminating oil, etc.) which it will yield will vary principally according to the different proportions of the members of a given series *present, but also through the varying proportion* of hydrocarbons of the different series. For a given range of boiling the naphthene and aromatic hydrocarbons have a higher density than paraffins, consequently a fraction from oil rich in these is of higher density than the corresponding fraction from a paraffinoid oil. Solid paraffins are said to be absent in Galician oils, and these oils (together with Roumanian) differ from most others in that the portions distilling below 150° are rich in aromatic hydrocarbons.

Two outstanding types of petroleum are met with, " paraffin base," and " asphalt base " oils. The latter are characterized by a medium or high percentage of asphaltum or bitumen, material of well-recognized character but the nature of which is little understood.

The presence of much asphaltum makes the oils dark coloured, increases their viscosity, and this concurrently renders it more difficult for water, dirt, etc., to separate out. Generally also asphaltic oils contain more sulphur than paraffin base oils. The latter may be free or almost free from asphaltum, but contain more or less paraffin wax. This wax distils in the refining process ; asphalt, on the other hand, is left in the stills and much comes on the market as petroleum pitch.

Whilst these are the two outstanding types of crude oil, a large proportion of oil is of a mixed base type.

Distillation of Petroleum. After the removal of adventitious dirt and water, by settling or centrifuging, the crude oil is submitted to distillation with the object of separating fractions having the desired characteristics for use as motor fuels, burning oils, intermediate oils, fuel oils, etc., the extent to which the distillation is pursued depending largely on the character of the crude oil and on market conditions. The technique of the distillation process has been immensely improved by the introduction of continuous distillation plants and the use of such efficient fractionating columns that products of the desired characteristics are obtained directly, thus avoiding re-fractionation. Beyond such an outline of the processes as will make clear the production of liquid fuels from the crude oil the distillation will not be described.

Broadly it may be said that the paraffin base oils, because of the high-grade lubricating oils and valuable paraffin wax they yield, are processed to what may be termed their ultimate commercial resolution, the motor fuel, burning oils (suitable for paraffin engines) and Diesel fuels being almost the sole fuels obtained.

The asphaltic oils, on the other hand, may be worked chiefly for the production of fuels, the "topping" process being employed. The heavy fuel oils may be left as a residue, comprising the bulk of the oil. Alternatively they may be put through the more elaborate process to give lubricating oils and a residue of fuel oil or asphalt. Mixed base oils may be treated by either alternative method; much will depend on their character and market conditions.

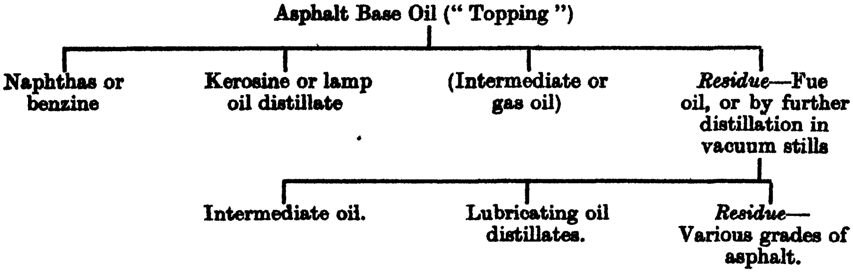
Broadly, whichever system is practised, the early stages of distillation yield the same types of product—gasoline or petrol (possibly in the first place as a naphtha or benzine), kerosines (burning and power distillates) and some intermediate or gas oil, the latter of importance as "Diesel distillate" fuels. Thereafter the lines of treatment diverge.

"Topping" is the simplest process for obtaining the three distillates leaving a residue which forms the bulk of the output of fuel or bunker oil. The process is simple, the crude oil being passed through heaters, where it is heated under pressure to a temperature high enough to cause all the lower-boiling components to volatilize when the hot oil is discharged into "evaporators" at atmospheric pressure. These mixed vapours pass first to air coolers and finally water-cooled condensers and condensation in order of diminishing boiling range takes place. The unvolatilized portion from the evaporators is the fuel oil. The distillates (naphtha, kerosines) will generally require re-fractionation, followed by chemical treatment, to be described later.

Where the more complete treatment for the wider range of products is practised, the first stage of distillation is at atmospheric pressure; the crude oil is heated and passed continuously to a fractionating column in which separation of fractions occurs at definite levels, the uncondensed vapours from the gasoline fraction alone passing away at the top to water-cooled condensers. The residue collecting at the bottom of the column is then further heated and discharged into a second fractionating column where a high vacuum is maintained. Lubricating oil fractions are obtained, of decreasing viscosity as the vapours are condensed higher and higher in the column, the vapours of the intermediate oils passing from the top to a condenser and residue fuel oils, or possibly asphalt itself collects at the bottom.

Diesel distillate oils are taken off with either system as fractions intermediate between the burning oils and the lubricating oils proper. For this reason these oils are commonly termed intermediate oils, and alternatively "gas oils" because of their wide use for carburetting blue water gas, and in small amount for the production of oil gas. Another most important use is in the "cracking" process.

The two alternative systems of topping an asphaltic oil are shown as follows:


Asphalt Base Oil (" Topping ")
Naphthas or benzine
Kerosine or lamp oil distillate
(Intermediate or gas oil)
Residue—Fue oil, or by further distillation in vacuum stills
Intermediate oil.
Lubricating oil distillates.
Residue—Various grades of asphalt.

" Cracking " distillation is a development designed to increase the yield of the more volatile products, more specifically the yield of motor spirit obtained from the crude oil. Higher-boiling hydrocarbons are not capable of being distilled at atmospheric pressure without decomposition. By increasing the pressure this decomposition is greatly increased, and, although losses through the formation of gases and coke are incurred, the process has proved invaluable in meeting the increased demand for motor spirit. Over 40 per cent. of the gasoline produced in the United States is " cracked " spirit.

The raw material is usually the intermediate or gas oil, but many " topped " residues are successfully cracked.

Cracked spirit differs in important ways from " straight " gasoline, and is dealt with in more detail on page 211.

Yield of Commercial Fractions from Crude Oils. Owing to the wide variation of crude oils of the same type and the different systems of distillation which may be employed, the yields of the various " fractions " can be only very generally given. In Table XXX a general average composition for typical crudes has been arrived at from several analyses published by the United States Department of Commerce :

TABLE XXX

DISTILLATION PRODUCTS OF PETROLEUM

	Paraffin base.	Mixed base.	Asphaltic base.
Naphthas (or benzine) . . .	36	23	—
Lamp oils (kerosines)	21	9	—
Intermediate oil (gas oil, Solar distillate)	12	20	11·2
Residue	31	48	88·8
Sp. gr.	0·823	0·880	0·979

It would not be correct to assume that asphaltic base oils generally do not yield naphthas and kerosines ; the example given is from heavy asphaltic types.

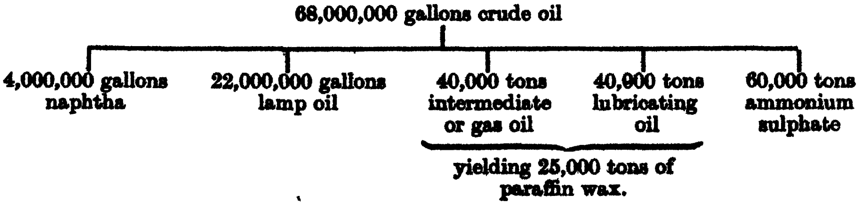
Refining Petroleum Fuels. Bunker or heavy fuel oil residues require no treatment other than is necessary to remove suspended solids and possibly water. Heavy oils, whether distillates or suitable residues, for use in internal combustion engines again are untreated beyond clarifying.

Motor spirit, special vaporizing oils and kerosines are usually slightly yellow and even if not so when first distilled, in course of time, especially on exposure to light and air, become yellow. Gum-like substances also are developed and these are very undesirable in these fuels. To remove these active substances treatment is necessary. Usually this consists in agitation with small quantities of sulphuric acid, followed by water and alkali washing. Another method used for motor spirit is treatment with a weak solution of soda, followed by sodium hypochlorite. Primarily this removes sulphur compounds.

Cracked spirit requires careful treatment, since it contains large proportions of unsaturated hydrocarbons, some of which, the di-olefines or diënes, are largely responsible for the changes subsequent to distillation, especially gumming. Less reactive unsaturated hydrocarbons, the olefines, are constituents of value. This makes the refining of such cracked spirit difficult, for whilst preserving as far as possible the harmless unsaturateds, those which form gum must be removed, and both are reactive to the reagents employed. After acid treatment of cracked distillates redistillation is necessary.

SHALE OIL

The production of shale oil is an important consideration in view of this being the only natural fuel oil of high quality which is produced in Great Britain. The bituminous shales which are employed are confined to a narrow strip of country between Edinburgh and Glasgow and on the Firth of Forth in the neighbourhood of Edinburgh. Considerable deposits of oil shale occur also in Dorset (the Kimmeridge shales) and in Norfolk, but the high percentage of sulphur in the oils distilled from these has precluded their development. Shales employed for distillation are also found in New South Wales and New Zealand. The distillation was established in Scotland originally by Young in 1849 for the production of burning and lubricating oils and paraffin wax. For many years approximately three million tons of shale were treated, with an average yield of 23 gallons of crude oil per ton. The quantity of the different commercial products obtained was:


68,000,000 gallons crude oil
4,000,000 gallons naphtha
22,000,000 gallons lamp oil
40,000 tons intermediate or gas oil
40,000 tons lubricating oil
60,000 tons ammonium sulphate
yielding 25,000 tons of paraffin wax.

The industry has, however, declined as the better seams became worked out, and in recent years the quantity retorted in Scotland has been about two-thirds of the above.

The process of distillation is a continuous one, the shale being fed into vertical retorts; the upper part of the retort is of iron, and this is heated to about 480° C. (900° F.), and the lower part of firebrick, this portion being heated to 700° C. (1300° F.). The hydrocarbons are all driven off before the residue, which amounts to 70–80 per cent. of the charge, passes into the firebrick part. This residue still contains from 9 to 14 per cent. of carbon and much nitrogen.

Steam is blown through the retort during distillation, and performs three important functions. The use of steam was intended primarily to prevent decomposition by heat of the valuable paraffin wax; it also plays an important part in the efficient recovery of ammonia, and in the gasification of the carbon present in the residue below the iron portion of the retort. Shale contains from 1·2 to 1·5 per cent. of nitrogen, and a notable proportion of this is in the above-mentioned residue, and without steam could not be recovered.

Passing from the still are the oil vapours, the steam, and about 2000 cu. ft. per ton of non-condensible gases. After condensation of the oil and steam these gases are generally utilized, together with producer gases, for heating the retorts.

Shale yields a very varying quantity of crude oil—from 18 to 40 gallons per ton, the average being 23 gallons. The specific gravity of the oil is between 0·860 and 0·890, and it usually solidifies at 90° F.

Crude shale oil differs in some respects from petroleum, chiefly in containing small quantities of the acids found in coal tar (cresols, etc.), and, being a product of destructive distillation in the first place, a high percentage of unsaturated hydrocarbons, of the character of those found in "cracked" petroleum oils. Consequently the refining required is more elaborate than for petroleum distillates and losses are high.

Two systems of treating the crude oil have been followed: (*a*) complete distillation to yield naphthas, burning oils, intermediate oils, lubricating oils and wax; (*b*) a topping method whereby the naphthas and burning oils are taken off, the residue oils being further distilled right down and the heavy distillate oils chilled, the wax separated, the liquid oils constituting a high-grade fuel oil, free from asphalt, and very suitable as fuel for compression-ignition engines. Scottish practice on the latter system has yielded the following: naphthas, 10; burning oils, 16; wax, 9; heavy fuel oil, 54 per cent. The loss, it will be noted, is 11 per cent.

It was only by the remarkable fuel economy practised, chiefly through the utilization of the considerable quantity of carbon in the spent shale as the source of producer gas for fuel purposes, together with the good recovery of ammonium sulphate, that the industry was able to compete successfully for many years with the supply of petroleum products. The position with regard to ammonium sulphate has, however, materially changed with the wide development of production of sulphate by synthetic methods and prices have fallen to unremunerative levels.

Although at present from these causes oil shales are not producing the quantities of oil formerly obtained, it is recognized in countries possessing supplies that in the future they will prove valuable sources of oil, and even in such a great oil-producing country as the United States, much attention is being given to the utilization of the oil-shale deposits.

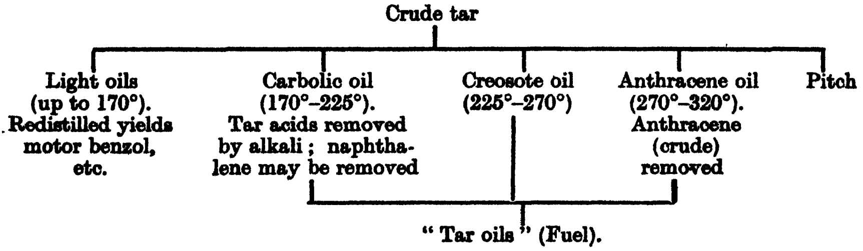
COAL TAR AND TAR OILS

The use of these materials in a country such as Great Britain is of considerable importance in the absence of a natural source of fuel oil. Should it become possible to adapt low-temperature tar or tar oils to the Diesel engine their value will certainly increase.

The more common forms of tar are those resulting from coal distillation in gasworks and coke ovens; in addition, considerable quantities are produced from blast furnaces working on hard coal, and minor quantities, which are important only locally, from all gas-producer plants working on bituminous fuels.

The physical characters and chemical components of tar are dependent largely upon the conditions of distillation of the coal. With high temperatures and the subjection of the products of distillation to a high temperature before escaping from the retort, as with the usual type of horizontal gas retort, the tars are very viscid and are highly charged with naphthalene and free carbon. With low-temperature tars, including those from blast furnaces using hard coal, the tars are fairly fluid, contain little naphthalene and anthracene, and practically no free carbon. In modern vertical continuous retorts the heat penetrates more slowly into the charge, and the distillation process is more or less intermediate between the above extremes, so that the tars are fairly fluid and do not contain so much naphthalene and free carbon, both of which are objectionable in fuel.

Tar Distillation. Crude tar to be used as a fuel must first be treated to make its flash-point suitable. This means the removal of 8–10 per cent. by distillation and the blowing of the residue with air to remove traces of volatile oils produced by cracking. Very little air-blowing is sufficient to give a heavy product having a flash-point of over 170° F. Such tars are heavy and viscous and lighter oils can be obtained by continuing the distillation to the pitch-point. The oils on the fuel range are those which boil approximately between 170 and 230° C. The commercial distillation of tar for the production of its valuable by-products need be dealt with only briefly. After separation of the ammoniacal liquor floating on the surface, the tar is distilled, usually in continuous systems although "pot" stills are sometimes employed. The following scheme represents generally the fractions obtained, and the range of temperature over which they are collected:


Crude tar
Light oils (up to 170°). Redistilled yields motor benzol, etc.
Carbolic oil (170°–225°). Tar acids removed by alkali; naphthalene may be removed
Creosote oil (225°–270°)
Anthracene oil (270°–320°). Anthracene (crude) removed
Pitch
"Tar oils" (Fuel).

As stated above, the middle fractions constitute the fuel oils. In the case of high-temperature tars such oils contain a high proportion of naphthalene and anthracene and are semisolid. When used as fuel it is therefore necessary to heat them to 40° C. to retain the solids in solution. Fluid and more easily handled fuel oils are produced by freezing out the solids and removing them by filtration.

The properties of typical tars and the yields of fractions obtained from them by distillation are given in Table XXXI, page 165.

There are certain essential differences between coal tar and tar oils and petroleum and shale oils. In the first place, a much higher proportion of oxygen-containing compounds, mainly constituting the tar acids, carbolic acid, cresylic acid, etc., are present. The effect of their presence is twofold; they detract seriously from the calorific value and produce pungent fumes during combustion, which may be troublesome in a badly ventilated stoke-hold. They are also corrosive and require special methods of handling to avoid damage to plant or to personnel. The ultimate composition of certain crude tars is approximately:

	Horizontal retort.	Vertical retort.	Low-temperature
Carbon	85·9	85·7	83·5
Hydrogen	6·3	6·3	8·5
Sulphur	1·2	1·6	0·8
Nitrogen	2·0	1·0	1·0
Oxygen, etc.	4·6	5·4	6·2

These tars were all produced from the same (Yorkshire) coal at the Fuel Research Station.

Secondly, tars may contain a high proportion of suspended solid matter in the form of free carbon which may prove troublesome in firing. Generally speaking, the proportion of free carbon increases with the temperature of carbonization and/or the amount of cracking to which the tar is subjected. The type of coal has also some influence. Representative amounts in different types of tar are as follows:

Kind of tar.	Free carbon per cent.
Low-temperature	0 to 1
Continuous vertical gas retort	5 to 10
Horizontal gas retort	8 to 15
Coke ovens, narrow	5 to 8
Coke ovens, wide	12 to 16

Thirdly, tar may contain water in suspension, which is separable only with difficulty. If this water tends to collect into globules it may give trouble in fuel burners. Although the amount, with good separation, may be as low as 0·5 per cent., it is more frequently 5–6 per cent.

The tars produced by low-temperature carbonization processes are very different from high-temperature tars. They are of lower specific gravity, more fluid, and contain practically no crystallizable solids such as naphthalene. They do contain, however, a higher proportion of tar acids and have therefore a somewhat lower calorific value. On account of their fluidity they can be regarded as directly suitable as fuel oil after a proportion of spirit has been removed to give the residue a suitable flash-point. If the tar is distilled to give tar oils these are also more fluid than the corresponding high-temperature tar products and contain no solids. To quote an example: a low-temperature tar was distilled up to 210° C. (yield 14 per cent.), a second fraction being collected from this point up to a residue of soft pitch—the oil amounting to 50 per cent. (by weight). The middle "tar oil" fraction had a specific gravity 0·996; Flash-point, 176° F.; Tar acids, 37·2 per cent., and a gross calorific value of 16,750 B.Th.U. per lb. (Fuel Res. Bd. Rept., 1930, 52).

An important consideration arising through the possible need of burning a mixture of tar oils and petroleum fuel oils is the liability of separation of pitch to occur. This invariably happens with any tars and may occur with tar oils unless these contain no substances insoluble in petroleum ether.

The use of tar oils as fuel in compression-ignition engines is further dealt with in Chapter XII (p. 248).

Physical Properties of Tar. The viscosity of tar and its specific gravity both vary with its nature, those tars prepared at lowest temperatures being lowest in both viscosity and specific gravity.

Calorific value varies within comparatively small limits about 16,000 B.Th.U. per lb.

The coefficient of expansion per degree F. varies a little, the mean figure being 0·00035.

The specific heat of tar varies from 0·30 to 0·40 calories per gram per degree C. (B.Th.U. per lb./° F.) at 40° C., and that of tar oils from 0·30 to 0·38 at 15–90° C.

Other properties are given in Table XXXI.

Brown Coal Tars and Tar Oils. There being no deposits of brown coal in this country, such oils are of no importance here, but with the large deposits in many parts of the Empire they may at some time become of value, although only a certain class of brown coal is capable of yielding the desired products, and this can be ascertained only by actual distillation. Generally, the character of the distillates obtained from suitable brown coals is similar to the shale products. The tars are paraffinoid, yielding both hard and soft wax, and a large proportion of the oil is well suited as a Diesel engine fuel.

The following yields have been given for Saxony lignite tar products: Naphthas, 2–3 per cent. (sp. gr. 0·780 to 0·810); burning oils, 2–3 per cent. (0·825 to 0·830); pale vaseline oil, 10–12 per cent.; gas oil, 30–35 per cent.; heavy vaseline oil, 10–15 per cent. The three latter oils are all suitable for internal combustion engine fuels.

Dolch (*Teer*, 1925 (No. 31), 510) gives the following data for eight brown coal tars:

		Mean.
Yield—per cent.	4·2–9·1	7·4
Specific gravity	0·982–1·036	1·032
Per cent. up to 150° C.	5–14	8·7
„ 150–200	6·5–12·5	9·2
„ 200–250	22·5–47·5	36·4
„ 250–300	17·5–21·5	19·7
Over 300	35·5–18	28·4
Tar acids in distillate to 300° C.	40·2–72·7	50·8

The composition of brown coal tar is given more fully by Metzger *Chemie d. Braunkohle*, 1927. Properties not given above are:

Solid paraffin content	15–19 per cent.
M. pt. of paraffins	46–48° C.
Naphthalene	0·01–0·07
Setting point of tar	50° C.

TABLE XXXI

Composition of Typical Dry Coal Tars

Percentages by weight.

Origin.	Specific gravity	Free carbon.	Tar acids.	Distillation range.				Pitch.	Naphthalene. Per cent.
				0–170° C.	170–230° C.	230–270.	270-pitch.		
Horizontal Retorts . . .	1·18	12	3·5	4	8	11	17	60	5
Vertical Retorts (20 per cent. steam) . .	1·10	4	9	3	16	10	19	52	1
Coke Ovens, narrow . . .	1·15	6	3	2	7	12	14	65	7
Coke Ovens, wide	1·20	15	4	2	3	7	17	71	5
Chamber Ovens.	1·15	3	5	2	9	12	15	62	1
Low Temperature (Fuel Research)	1·06	1	12	6	16	12	31	35	trace
Blast Furnaces Producers	1·10	—	3	1	2	9	25	63	trace
Water-Gas . .	1·04	1	nil	10	17	27	21	25	2

CALORIFIC VALUE OF HEAVY FUEL OILS

Petroleum. Being complex mixtures of many hydrocarbons, some variation is found in the residue oils from different crudes, and little value would result from enumerating the calorific value of individual fuel oils. Very rarely will it be found that the calorific value (gross) is outside the following: minimum, 10,500 calories per gm. (18,900 B.Th.U. per lb.); maximum, 11,000 calories per gm. (19,800 B.Th.U. per lb.)

It is important to note that the effective calorific value of fuel oil is reduced by the presence of water, not only as an effect of dilution but also by the amount of heat required to evaporate this water. The latter effect is equivalent to 13·14 B.Th.U. per lb. for each 1 per cent. of water. The effective calorific value of a wet oil is therefore:

$$\frac{\text{Cal. value of dry oil} \times (100 - H_2O\%)}{100} - (13{\cdot}14 \times H_2O\%).$$

Gas Tars. The following calorific values are stated to be the average for dry tar by the authorities named: 9000 cals. (16,200 B.Th.U.), Godinet; 8800 cals. gross (15,840 B.Th.U.) and 8530 cals. net (15,400 B.Th.U.), Mahler; 8510 cals. gross (15,350 B.Th.U.), Euchêne. The German Gas Association takes a value of 8800 cals. (15,840 B.Th.U.).

From a number of determinations of the calorific value of horizontal and vertical retort tars it will appear that the latter, besides being less viscous and containing less water and free carbon, have the higher calorific value, the mean figures for the dry tars being: horizontal, 9115 cals. (16,430 B.Th.U.); vertical, 9,300 cals. (16,740 B.Th.U.).

Tar Oils. As indicated on page 163, these are obtained from the carbolic, creosote, and anthracene fractions of high temperature tars, the creosote fraction being seldom treated in any way. Varying amounts of tar acids (up to 25 per cent.) may be present. Naphthalene is also present in varying amount; high percentages cause separation at moderate temperatures.

The specific gravity is between 1·02 and 1·06; the *gross* calorific value usually lies between 16,560 and 16,850 B.Th.U.; the *net* calorific value between 15,840 and 16,200. From 25 samples G. N. Huntly gave a range of 14,960–17,860 B.Th.U. *gross*, with an average of 16,730 B.Th.U.

The ultimate composition of dry and ash-free tar oils is: Carbon, 87–89·5; hydrogen, 6·5–7·5; oxygen and nitrogen, 3·0–5·0; sulphur, 0·5–1·0 per cent. A typical low-temperature tar-oil is stated (Report of Director of Fuel Res., 1930, 52) to contain: Carbon, 84·7; hydrogen 9·0; sulphur, 0·8, and oxygen and nitrogen 5·5 per cent. and to have a calorific value of 15,800 B.Th.U. per lb.

The removal of tar acids from tar oils raises their calorific value by about 35 B.Th.U. for each 1 per cent. of acids removed.

THE PRODUCTION OF FUEL OILS BY HYDROGENATION

Fuel oils and motor spirit can be produced by the treatment of coal and its products at high temperature and pressure in the presence of hydrogen (hydrogenation). When coal is carbonized it gives a yield of tar amounting to only 8 to 10 per cent. of the coal. When treated by the hydrogenation process, however, a crude oil amounting to about 75 per cent. by weight of the coal treated is obtainable. The hydrogenation of coal therefore offers a means of producing supplies of oil from coal in countries where natural sources of oil are not available.

The pioneering work in the treatment of coal was that of Bergius, who erected in 1924 an experimental plant at Mannheim, Germany. In 1926 a duplicate plant was installed at the Fuel Research Station, London, in order to determine how applicable the process was to British coals. Developments took place in Germany, particularly in the treatment of brown coal and brown coal tar, and it is reported that during 1932 as much as 350,000 tons of motor spirit were produced in this way. During the same period a programme of work was started by Imperial Chemical Industries, Ltd., which resulted in the construction and operation of a 15-ton-per-day plant. From the experience gained with this plant the Company are erecting a plant to treat 400 tons of coal per day.

Bergius Process. In the Bergius process 20 parts of coal (less than 2 mm. in size) were mixed with 8 parts of heavy tar and 1 part of " luxmasse " (to fix the sulphur as iron sulphide) and the pasty mixture was pumped through three horizontal converters in series, 6½ ft. long by 8 in. internal diameter with 2½ in. walls and fitted with stirrers. The temperature was kept at 450–480° C. under a hydrogen pressure of 200 atmospheres. The product leaving the last converter was a thick tarry liquid containing as a stable emulsion water, luxmasse and residual solid matter from the coal. The products obtained from a Yorkshire coal containing 7·2 per cent. of ash and 0·9 per cent. moisture were:

TABLE XXXII

YIELDS FROM BERGIUS PROCESS PER TON OF PURE COAL

Hydrogen Consumed = 114 lb.

Fraction	0°–175°	= 83 lb.
,,	175°–230°	= 208 ,,
,,	230°–270°	= 197 ,,
,,	270°–310°	= 105 ,,
,,	310°–360°	= 208 ,,
Pitch		= 329 ,,
Gas Benzine		= 42 ,,
Residual Gas		= 325 ,,
Unconverted Coal		= 363 ,,
Water		= 179 ,,
Coal Ash		= 161 ,,
Loss		= 154 ,,
		2354

The total yield of 52 per cent. of heavy oil represented 28 gallons of motor spirit, 40 gallons of light fuel oil, and 52 gallons of heavy residual oil per ton of coal.

Modern Process. Coal in admixture with heavy oil and catalyst is pre-heated with hydrogen in an apparatus similar to a pipe still and delivered into the first-stage converter (a tall vertical cylinder) at a pressure of 250 atmospheres. The effect of the catalyst is to accelerate the reactions in the direction of hydrogenation and reduce those of cracking or carbonization. The time of treatment is about two hours. The main product escapes as vapour to a condenser from which it is collected and distilled to yield crude spirit, middle oil, and heavy oil. A stand-pipe within the converter allows of the removal of the heavy sludge, which on distillation yields heavy oil and a solid residue which forms a boiler fuel. The heavy oil from this sludge and that obtained by distillation of the main product, is used for mixing or pasting fresh coal. Alternatively, the entire product may leave the converter at the top and be separated by fractional condensation into the same three fractions. In this case the distillation is done under a pressure of 10–12 atmospheres in order to retain volatile hydrocarbons as liquid products. The spirit from the main product is passed forward for refining, and the middle oil is treated in the second or vapour stage converter with additional hydrogen for the production of motor spirit and/or fuel oil. In this stage the catalyst is pelleted or supported by a porous material within the converter. The process as a whole can be run so as to produce motor spirit only, or motor spirit and various grades of oil including lubricating oil. The total yield is of the order of 165 gallons per ton of dry ash-free coal. The properties of the spirit and fuel oil as indicated by Fuel Research Station experiments are:

TABLE XXXIII

PROPERTIES OF HYDROGENATION SPIRIT AND OIL

	Hydrogenation spirit.	"Straight" motor spirit.	Fuel oil.
Specific Gravity	0·78	0·74	1·048
			Ig. Temp. 397° C.
Distillation			
0°–100° C.	40	43	
100°–200° C.	58	55	C.V. 17,540 B.Th.U.
Gum after 1 year (bottled) .	17 mg./100 c.c.		C. 89·2 per cent.
H.U.C.R.	6·4	5·4	H. 8·2 „
Octane No.	88	68	
Aromatics	24	—	
Unsaturateds	7	—	
Saturateds	41	—	
Naphthenes	28	—	

The spirit is a satisfactory motor spirit for general use, but the fuel oil is satisfactory only for slow-running Diesels and less suitable, on account of its high aromatic content, for high-speed Diesel engines.

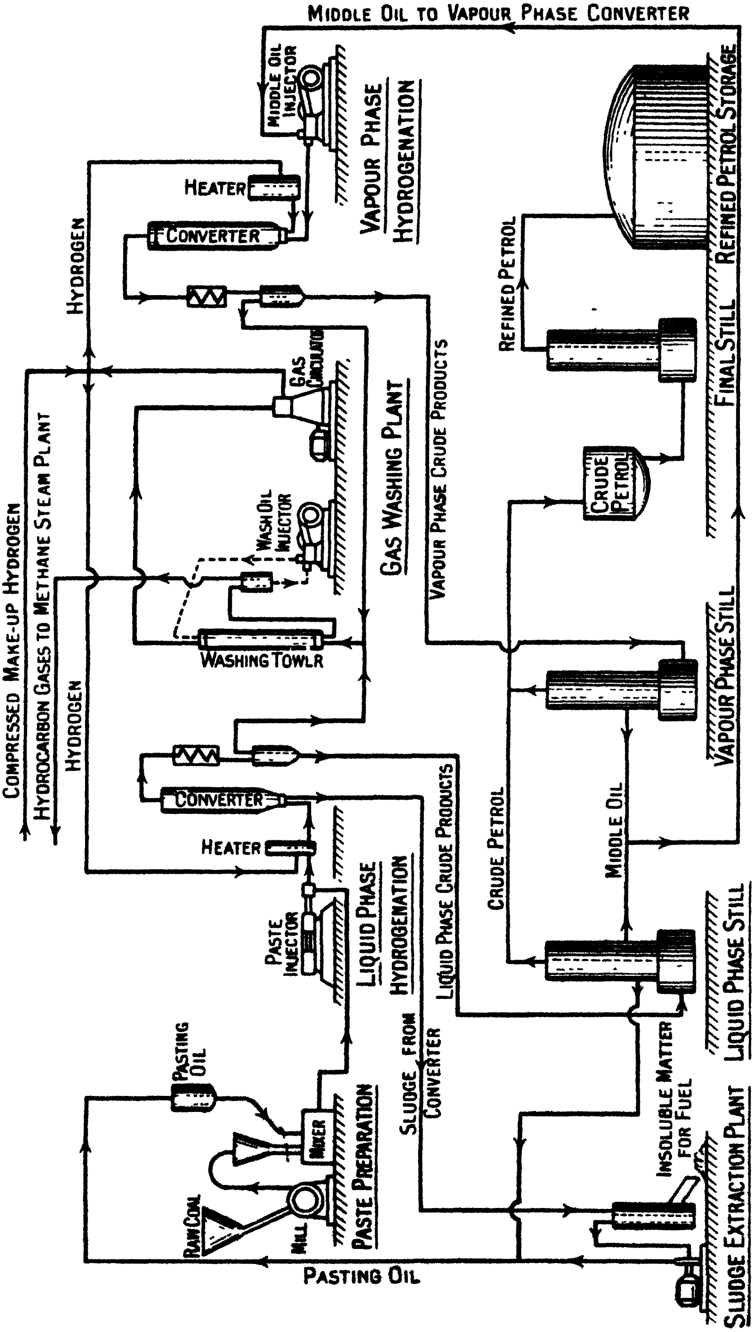


FIG. 20.—Flow Diagram of Hydrogenation of Coal Plant and Refining.

The flow diagram (Figure 20) gives some idea of the complexity of a complete hydrogenation plant. This diagram was described by Gordon (*Trans. Inst. Min. Eng.*, 1931, **82**, 348), but does not necessarily describe the plant to be erected by Imperial Chemical Industries. The steps in the process can be followed easily and represent (i) liquid-phase hydrogenation of coal paste, (ii) distillation or fractional condensation of the product to crude spirit, middle oil, heavy oil and sludge, (iii) vapour-phase hydrogenation of the middle oil, (iv) collection of the crude spirits from both phases and (v) recycling of heavy oil with the coal and of middle oil in the vapour-phase converter. An idea of the magnitude cf the plant can be obtained by visualizing the converters as steel vessels 5 to 6 ft. in internal diameter and 40 ft. in height, and having a capacity of about 2 tons of coal or 3 tons of middle oil per hour. An interesting account, by Dr. M. Pier, of the I.G. Luna plant for the hydrogenation of brown coal will be found in *The Industrial Chemist* (1935. April, p. 139). When in full operation it is estimated that more than 300,000 tons will be treated annually.

A flow diagram of the same type, representing the process adopted in Germany for the hydrogenation of brown coal tar is given in Figure 21 as described by Foster (*Petroleum News*, 1930, **22**, No. 33). In this flow diagram two reaction stages are shown. In the first the crude tar is treated with a dispersed catalyst at 850° F., the product is separated by distillation into spirit and oil and the latter re-treated at 950° F. over a vapour-phase or " suspended " catalyst. It is noticeable that in both stages the oil and hydrogen are separately pre-heated to as high as 800–900° F. In this process it is claimed that from 100 parts dry tar and 8 parts of hydrogen 85 parts of " gasoline " can be produced. The composition of this motor spirit is stated to be : unsaturateds 3·4, aromatics 15·0, naphthenes 30·0, paraffins 51·6, and its boiling range to be from 142° to 390° F. (60–200° C. approx.).

The Hydrogenation of Coal. It has been shown that satisfactory conversion can be achieved in the case of all British bituminous coals but that ease of hydrogenation and yield of oil varies with the type of coal. The best results are obtained with coals of carbon content varying from 80 to 84 per cent. and hydrogen content from 5·0 to 5·8 per cent. Coals of lower carbon content (higher oxygen content) give lower yields of oil. Coals of higher carbon content are more difficult to deal with, requiring higher temperatures and a longer time of treatment. For this reason the yield of gaseous hydrocarbons is higher and of oils less. At the Fuel Research Station, E. Kent coal (30 per cent. volatile matter and containing 87·5 per cent. of carbon) has been successfully treated to give an oil yield of 71 per cent.

To test coals is a relatively simple matter, the coal is heated with hydrogen in a 2-litre converter under standard conditions and the pro-

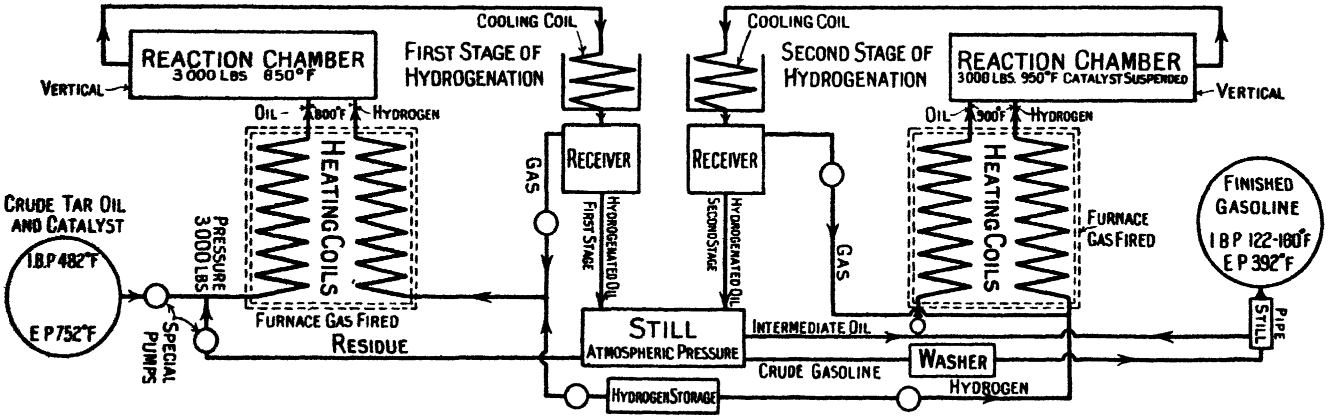


FIG. 21.—Flow Diagram of Hydrogenation Plant for Brown Coal Tar.

ducts are removed and analysed. The critical quantities which are measured are (1) residual solid matter, (2) oil soluble in chloroform, and (3) hydrogen reacting. The following examples emphasize the wide suitability of British coals:

	Non-coking bit. steam.	Yorkshire steam.	Lancs. coking.	N. Staffs coking.	Kent coking.
Carbon . . .	78·7	83·5	82·0	85·1	87·5
Hydrogen . . .	5·6	5·5	5·4	5·6	5·3
Solid matter . .	7·7	10·4	5·6	9·4	18·2
Soluble oil . .	70·3	73·4	72·4	74·6	71·0

In the first stage where coal is converted to heavy oil a catalyst is necessary. In order to discover a suitable catalyst for the conversion of coal into heavy oil practically all inorganic substances have been examined. It has now been established that certain elements of the fourth group of the periodic classification are the most active; these are titanium, germanium, tin and lead, the first only in conjunction with iron. Zinc is also active, and iodine would be valuable if its effect in other ways could be controlled. The failure of nickel oxide, a well-known hydrogenating catalyst, is explained by the fact that it is easily poisoned by sulphur. In some forms, i.e. nickel oleate, this element is however, still active. Of the above, it is indicated that the organic compounds or salts of tin are the most active, and the amount which it is necessary to add to the coal is appreciably less than 0·1 per cent. It is an interesting fact that the inorganic matter of certain coals contains elements which are active catalysts, i.e. germanium, and it may be possible that certain coals would be particularly amenable to hydrogenation treatment on account of the inorganic matter contained in them.

In the second stage of the process, where the middle oil is converted to oils of lower boiling-point, the catalyst is different. The best general catalysts are compounds of molybdenum and tungsten, probably the di-sulphides. Iodine again would be a satisfactory catalyst for this stage, if its other effects could be controlled. The Fuel Research Station have shown (King and Matthews, B.P. No. 410, 771) that a granulated material such as bauxite or aluminium gel is a very satisfactory means of supporting the catalyst. Since fresh catalyst is not being added continuously, in this case the activity of the charge may deteriorate owing to the deposition of asphaltic bodies. These are readily removable by oxidation with air, when the catalyst regains its initial activity. Deterioration is largely prevented by cutting the distillation of the middle oil at 320° C. and allowing no time for polymerization between distillation and treatment. The action of the catalyst in the conversion of coal is easily illustrated by pressure temperature curves, Figure 22, obtained in a static converter in the presence of the catalyst. The curve turns downwards, showing the interaction of hydrogen at a much lower temperature in the presence of catalyst than in its absence.. Similar experiments (Horton, King and Williams (*J. Inst. Fuel,* 1933, **7**, 85) in which the rate of production of liquid products from coal was measured show that the rate is accelerated by the presence of a catalyst, and that the action of the

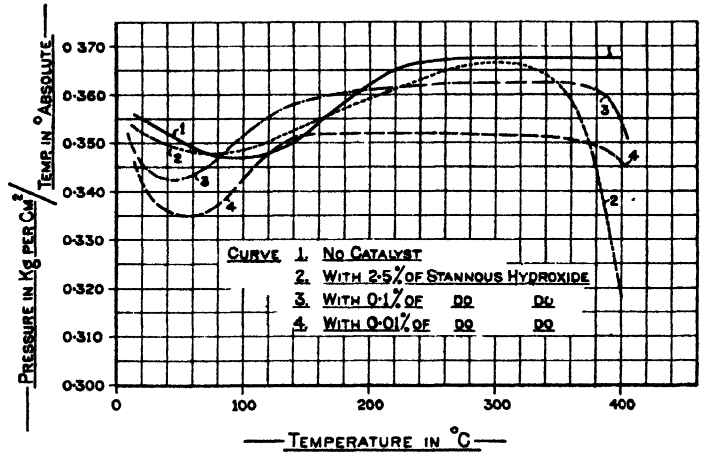


Fig. 22.—Effect of Temperature on P/T in the Hydrogenation of Coal.

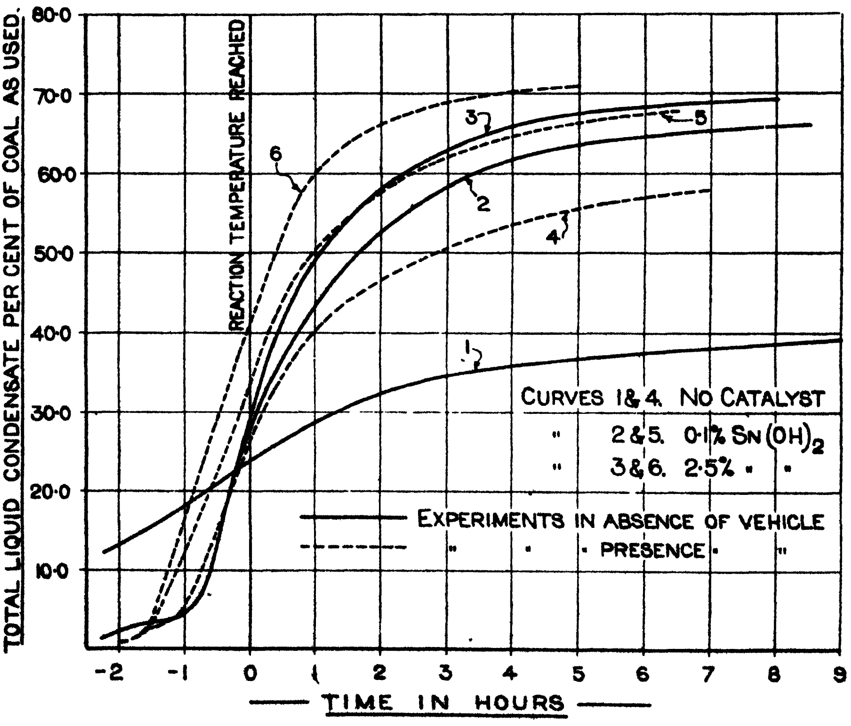


Fig. 23.—Rate of Production of Liquid Product from Coal.

catalyst is greatest in the earliest stages of treatment. Rate of production curves are shown in Figure 23.

Curve 1, obtained in the absence of a catalyst, shows a slow rate and total yield of less than 40 per cent. The increase of rate caused by a catalyst (curve 3) is marked and the final yield of almost 70 per cent. is much higher. The curves also show the beneficial effect of the presence of a liquid medium or vehicle. In the absence of a catalyst (curve 4) the advantage over dry coal (curve 1) is marked. The value of the catalyst in the presence of a vehicle is therefore less marked but is none the less important in preventing the interference of cracking reactions.

Hydrogen. Hydrogen is required for both the first and the second stage treatments. Much of this hydrogen is absorbed, but a portion forms gaseous hydrocarbons. If the process is to be self-contained, these must be reconverted to hydrogen of sufficient purity to avoid wastage. Perhaps the cheapest process for the manufacture of hydrogen on a large scale is the interaction of water gas with steam, so that the carbon monoxide of the former is oxidized to carbon dioxide, giving an equal volume of hydrogen. This, with the original hydrogen of the water gas, is freed from carbon dioxide by washing with water or an aqueous solution of triethanolamine $N(C_2H_5O)_3$ at a pressure of 250 lb. It is claimed that a 50 per cent. aqueous solution of this substance will dissolve 60 times its volume of carbon dioxide at 35° C. and atmospheric pressure. The dissolved gas can be removed and the solution regenerated by heating.

It is stated that hydrogen can be prepared on a large scale by this process at a cost of about 9*d*. per thousand cu. ft. Since coal requires 10 per cent. of hydrogen, or 35,000 to 40,000 cu. ft. per ton, the cost if only fresh hydrogen were used would be about 26*s*. to 30*s*. per ton of coal treated or 2¼*d*. per gallon of spirit produced.

The gas leaving the plant contains 70–80 per cent. of hydrogen, the remainder being mainly gaseous hydrocarbons formed in the process. This gas can be washed with oil under pressure to remove the hydrocarbons, and these can be converted into hydrogen by interaction with steam in a separate process.

The reactions are:

$$(1)\ CH_4 + H_2O = CO + 3H_2 - 50{\cdot}7\ \text{cals.}$$
$$(2)\ CO + H_2O = CO_2 + H_2$$

Reaction (1) takes place at a temperature of 1000° C. and a pressure of 2–3 atmospheres in the presence of a nickel catalyst and reaction (2) at 800–1000° C. in the presence of an iron oxide catalyst.

The importance of these reactions is obvious since by their use the hydrogen necessary for the process can be recovered from the spent gases from the converters and, if the conditions of operation are so arranged as to yield a sufficient quantity of gaseous hydrocarbons the process could be made self-contained. This stage is reached when the amount of gaseous hydrocarbons is about 35 per cent. of the coal treated. In such a case fresh hydrogen would be necessary only at intervals to purge the plant from accumulated nitrogen. It is probable that a compromise will be reached in practice by the supply of a proportion of fresh hydrogen so as to permit of running the plant to give a maximum production of oil. It has been found in experimental work that the purity of hydrogen necessary for the first stage converter should be about 85 per cent.; leaving the converter it would then be about 70 per cent. In the second stage converter the concentration of hydrogen must not be less than 90 per cent. entering the converter.

Experimental Results. In order to illustrate the yields, etc., obtainable by the hydrogenation of coal the following results, Table XXXIV, are quoted from experiments which have been carried out at the Fuel Research Station.

The results are quoted in terms of dry, ash-free coal and show the liquid- and vapour-phase results separately. In the liquid phase 165 gallons of heavy oil are produced per ton of coal with a consumption of 24,000 cu. ft. of hydrogen. When the middle oil has been converted to spirit the total hydrogen consumption is 48,000 cu. ft. and the yield of oil has been reduced to 123 gallons. On a manufacturing scale this yield is almost certain to be exceeded and Gordon (*Gas J.*, 1931, **195**, 217) claims 165 gallons per ton of pure coal, i.e. 62 per cent. by weight of the coal. The spirit produced is characterized by a high anti-knock value (octane number 88) owing to the presence of 24 per cent. of aromatics. Gordon, in another paper to the World Petroleum Congress of 1933 (*Petrolem Times*, 1933, **30**, 219) gives further particulars of the properties of the spirit and oils. He states that hydrogenation spirit requires very little refining; one wash to remove dissolved hydrogen sulphide, one to remove traces of phenols and, in the case of aromatic spirits a wash with sulphuric acid to remove gum-forming constituents. The vapour-phase stage of the process can be controlled in terms of temperature, pressure and catalyst to give either an aromatic spirit of high anti-knock value and rather low volatility or a naphthenic spirit of higher volatility. Normally, the end product of the whole process would be a suitable blend. This blend is very stable and remains water-clear when stored over long periods.

The middle oil produced from the liquid phase, i.e. direct from the coal, forms a satisfactory fuel oil, carbon 90·1, hydrogen 8·4, nitrogen 1·1, sulphur 0·2 per cent., having a calorific value of 9736 cals. per gm. (17,500 B.Th.U. per lb.). Its viscosity is 785 sec. at 0° C. (Admiralty) and its flash-point 280° F. (Pensky-Martens). A paraffinic Diesel oil has

TABLE XXXIV

Results of Hydrogenation of Beamshaw Coal

Hydrogenation Temperature, ° C.	450
Hydrogenation Pressure, Atmospheres	200
First Stage in Liquid Phase:	
Hydrogen reacting, cu. ft. per ton a.f.d. coal	24,000
Yields:	
Spirit, b.p. $< 200^\circ$ C. galls. per ton a.f.d. coal	30
Oil, b.p. $> 200^\circ$ C. ” ” ” ”	135
∴ Total oil ” ” ” ”	165
Second Stage Treatment in Gas Phase, of Oil b.p. $> 200^\circ$ C. produced in First Stage:	
Hydrogen reacting, cu. ft. per ton a.f.d. coal	24,000
Yields:	
Spirit, b.p. $< 200^\circ$ C. galls. per ton a.f.d. coal	110
Oil, b.p. $> 200^\circ$ C. ” ” ” ”	13
∴ Total oil ” ” ” ”	123
Combined Figures for the Two Stages:	
Hydrogen reacting, cu. ft. per ton a.f.d. coal	48,000
Yields:	
Spirit, b.p. $< 200^\circ$ C. galls. per ton a.f.d. coal	140
Oil, b.p. $> 200^\circ$ C. ” ” ” ”	13
∴ Total oil ” ” ” ”	153
Properties of Spirit from Combined Stages:	
Distillation:	
Fraction b.p. $< 100^\circ$ C. per cent. of spirit	40
” b.p. 100°–200° C. ” ” ” ”	58
Specific gravity at 15° C.	0·78
Octane number	88
Composition:	
Aromatics per cent. of spirit	24
Unsaturateds ” ” ” ”	7
Saturateds ” ” ” ”	41
Naphthenes ” ” ” ”	28

not yet been produced, but a naphthenic oil of fairly satisfactory properties could be produced in place of a proportion of spirit. The ignition temperature of such an oil is stated to be 265° C. (Moore).

It is impossible to calculate costs from experimental data, but it has been stated by Imperial Chemical Industries, Ltd., that motor spirit can be manufactured by the combined process at a price of 7*d.* per gallon. Since this price cannot compare with that of imported petroleum spirit, it is apparent that hydrogenation is a paying proposition only when protected by the existence of a substantial tariff on imported spirits. Also, it is improbable that the process can compete with the production of fuel oil while petroleum fuels are obtainable at about £3 per ton.

The Hydrogenation of Tars and Tar Oils. Low-temperature tars and tar distillates are amenable to the treatment given in the second or vapour-phase converter of the coal hydrogenation process. Using the same catalysts experiments at the Fuel Research Station have shown that it is possible to produce from low-temperature tar 101 gallons of motor spirit per 100 gallons of tar treated, consuming in the process 18,000 cu. ft. of hydrogen. Low-temperature tar distillates and high-temperature tar distillates are even more amenable to treatment, and consume less hydrogen. Gas-retort or coke-oven tar cannot be treated in one stage as their distillates and low-temperature tar can, but by introducing a preliminary pressure-cracking stage in the presence of hydrogen, the volatile fraction can be treated in the vapour phase so as to give a yield of spirit equal to 75 per cent. of the tar. From the pressure-cracking stage a quantity of pitch-like material is also available and may have some commercial value.

The main results of the treatment of tar and tar oils and the properties of the products are contained in Table XXXV, again quoting from results obtained at the Fuel Research Station.

TABLE XXXV

HYDROGENATION-CRACKING OF TAR AND TAR OILS

Raw Material.	Low-temperature Tar.	Low-temperature tar oil.	High-temperature Creosote.
Temperature of reaction . . .	450–480	480	480
One Treatment of the Raw Material:			
Yields of Products, per cent. by volume:			
Spirit to 200° C.	55	84	72
Oil above 200° C.	53	19	40
Hydrogen absorbed, cu. ft. per 100 gallons raw material	9000	8500	12,000
Complete Conversion of the Raw Material to Spirit:			
Yields of Products obtained, per cent. by volume of raw material:			
Spirit to 200° C.	101	99	106
Hydrogen absorbed, cu. ft. per 100 gallons raw material	18,000	10,000	16,000
Properties of the Spirit:			
Specific gravity at 15° C.	0·810	0·800	0·830
Analysis, per cent. by wt.:			
Aromatic hydrocarbons	33	33	49
Unsaturated hydrocarbons . . .	2	2	3
Saturated hydrocarbons	65	65	48
Amount of spirit below 100° C. per cent. by volume	17	18	18
Octane Number	75	75	80

Low-temperature tar yields 101 gallons of spirit per 100 gallons of tar with a consumption of 18,000 cu. ft. of hydrogen. The spirit has a good octane number ($>$ 75), but the proportion boiling below 100° C. is rather low. This could however be controlled by modifying the catalyst used. Distillates from low-temperature or high-temperature tars give equally satisfactory yields of good spirit and are more easy to deal with in the process.

The Hydrogenation of Petroleum Residues. The residue oils and bitumens from petroleum stills, or the heavy residues from cracking plants, can be successfully hydrogenated, the asphalts being completely converted into liquid products. This treatment greatly enhances the value of these residues. Similarly gas oils, instead of being simply cracked, may be hydrogenated in the vapour phase. The gasolines have an exceptionally high octane number ($>$90) and, contrary to "straight" and "cracked" gasolines, their higher boiling fractions have the best anti-knock characteristics.

CHAPTER IX

OIL FUEL BURNING

INDUSTRIAL SYSTEMS

General Arrangement of Oil Supply to Burners. The oil should be almost free from suspended water and solids, but most installations provide for the contingency of this not being wholly the case: When the oil is supplied by gravity from tanks it is usual to employ a pair of supply tanks into which the oil is pumped ; here it is heated by a steam coil to promote the separation of water and increase the fluidity of the oil.

At ordinary temperatures the separation of finely divided water is very sluggish, since the difference of gravity is but slight, and with the high viscosity of the oil these globules remain suspended almost indefinitely. On heating the oil two distinct changes occur—first, its viscosity is reduced very rapidly, and secondly, the oil expands at a greater rate than water, so that the difference in specific gravity is considerably increased. The relative coefficients of expansion of heavy oils and water are approximately per degree Centigrade 0·00070 and 0·000476 ; or per degree Fahrenheit 0·00039 and 0·000264.

It is important that condensed water from the heating coils must not be allowed a direct return into the boiler feed, otherwise a leak in the coils would allow of oil getting into the feed. To provide against this the condensed water from the coils must be collected in a tank where it can be seen whether or not it is free from oil, and an efficient oil separator should be provided.

The settling tanks must be provided with suitable vents and in the case of large steamships a capacity equal to several hours' supply to the burners must be allowed for each. By the Board of Trade regulations (for passenger ships) the tanks must be tested to 15 lb. per sq. inch. The rate of separation of water from oil is accelerated by heating the oil, the best temperature may be as high as 180° F.

The temperature to which the oil may be heated safely before delivery to the burners is limited obviously to some degrees below the flash-point, and it is very essential to the attainment of smooth working, with the least necessity for alteration of the oil or atomizing agent valves, that the temperature shall be fairly uniform and the pressure of the oil supply constant. To this end thermometers should be placed in the supply pipe.

When steam or air atomization is employed the supply of oil may be from a feed tank or tanks at a sufficient height to give the necessary flow. Since very viscous oils cannot be effectively atomized heating is necessary and where steam is available a suitable heater may be arranged in the supply line. Where this is not the case some special arrangement must be made, thus a small boiler fired with a paraffin vapour lamp, or in shore installations by coal gas may be used. Electric resistance heaters have also been used. Straining of the heated oil is also desirable.

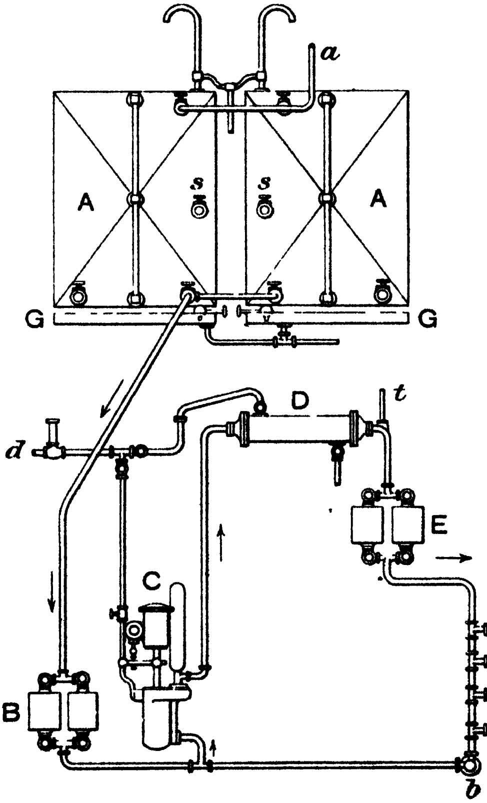


FIG. 24.—Körting Pressure System.

A A, Oil settling tanks.
a, Oil supply pipe.
G G, Drip trays.
B, Duplicate suction strainers.
C, Oil pump with air pressure vessel.
D, Oil heater.
E, Duplicate discharge strainers.
F, Pipes to burners.
b, Bye-pass valve.
t, Thermometer.
d, Steam supply to pump and heater.

In pressure-spraying systems filters are provided in duplicate on both the suction and pressure sides of the oil pump, the gauze in the filters in the suction side being of larger mesh than that in the pressure side, the actual mesh of the gauze being determined by the fluidity of the oil used.

Instead of these simple gauze filters other and more efficient methods of removing solid matter are available, such as the well-known " Streamline " filters or the " Auto-Klean " filters. In the latter the oil passes from outwards between a number of perforated thin steel plates, with fine clearances between them. Between the plates are a number of thin fixed steel knives. On giving the filtering cartridge a half-turn the accumulated dirt is cleared away and falls into a sump from which it is readily removed. To provide for the proper regulation of the oil pressure a loaded valve on a connection between the pressure side and the suction side of the pump is fitted, and lifts when the maximum is reached. For the oil to attain the necessary working temperature it is circulated through suitable heaters by piping leading from the oil supply pipe to the burners (which are shut off) back to the suction side of the pump.

The general arrangement in the different systems is very similar, and is illustrated in Figure 24 for Körting plant.

Provision against Fire. On board ship provision is usually made to deal with any outbreak of fire and special regulations for this were laid down by the Board of Trade (1920) for passenger-carrying steamships fitted for oil fuel. These included the provision in each stokehold of 10 cu. ft. of sand, sawdust impregnated with sodium bicarbonate or other suitable material. Further, that steam could be discharged into the lower parts of any boiler-room, the valves being arranged so that they could be operated from outside.

One of the most effective methods of dealing with burning oil is the use of some form of " foam " extinguisher, and the Board of Trade Regulations, although not making such provision compulsory, strongly recommended the provision of a " foam " plant, again controlled from outside.

Vaporizing and Spraying the Oil. For the complete combustion of the oil it is essential that as perfect a mixture as possible with air shall be attained. On theoretical grounds this is accomplished most easily with the oil vapour, but it is not practicable to vaporize properly the heavier fuel oils, since the temperature requisite leads to " cracking " of the oil and the formation of carbonaceous deposits in the vaporizer and burning of the metal. The system however is applicable with low boiling oils, such as kerosine and intermediate oils, and little trouble is experienced if the vaporization takes place in presence of a good volume of air.

With the heavier oils such as are generally employed, conversion into as fine a mist of oil globules as possible enables proper admixture of air to be attained, and various forms of sprayers or atomizers are employed.

These may be classified in two main groups: (*a*) those in which air or steam under pressure break up the oil; (*b*) those which are essentially mechanical, and these again may be grouped under (1) those where the oil is forced at pressure through suitable orifices, (2) broken up by some such device as a baffle or rotating propeller, (3) those dependent on a rotary motion imparted to the sprayer. The two latter types are seldom employed, but all the well-known types of sprayers may be relied on to give the necessary disintegration, and as far as this effect is concerned there is but little to choose between the different systems. It is upon other considerations, dealt with later, that the selection of the particular system mainly depends. Whilst an efficient sprayer is essential, attention to the details of the installation as a whole, and more particularly the air supply, is the most important factor for good results.

The number of sprayers which have been designed is legion, and only typical examples of established efficiency are described below, but here it may be mentioned that with any pattern it is essential that the burner should not get heated unduly over any great part of its length. The sprayers are frequently arranged on a swinging arm so that they may be turned clear of the furnace, the oil and steam or air supply being cut off at the same time. This enables inspection and cleaning of the burners to be made, or, where solid fuel is sometimes employed as an alternative, the burners to be turned out of the way without the necessity of dismantling.

Well designed sprayers will give a practically uniform distribution of the oil globules throughout the cone of spray and ensure that no large diameter globules are present, for these will probably not be burnt completely whilst in suspension.

STEAM AND AIR SPRAYERS

Essentially the principle is the same for either steam or air, namely the provision of the atomizing agent at such a pressure, according to the design of the sprayer, that a mist of oil particles is produced. Suitably designed sprayers will operate with either medium.

With steam the fact that, in boiler practice, a convenient working fluid under steady pressure is at hand for spraying the oil, accounts for its extensive employment and the large number of successful steam sprayers which are in use. Broadly, these may be divided into two groups—those in which the oil and steam escape through concentric circular orifices, and those in which straight slots are employed, but the latter are practically obsolete. In many of the former elaborate arrangements are made for further heating the oil in the burner by suitable jacketing. It does not appear that any great advantage arises from this; indeed, some of the simplest burners give the best results in practice, and complication of design is to be avoided.

The steam for atomizing should be dry and preferably superheated. For starting up the small amount of steam necessary must be raised in some type of small auxiliary boiler.

With air injection, unless compressed air is available, some form of blower must be provided, and this may be driven directly by an electric motor or from line shafting.

Urquhart's Sprayer. For medium air or steam pressure Messrs. Urquharts have two or three designs of burners, the one chosen for illustration (Figure 25) being suitable for industrial plants and steam-raising. The oil capacity is from 10 to 500 lb. per hour, with air or steam pressure between 5 and 30 lb. per sq. inch. For these burners it is claimed that a high degree of atomization is possible with a minimum volume and pressure of air (or steam), and because of this no special brickwork in the furnace is required, beyond, of course, closing over grate bars if existent.

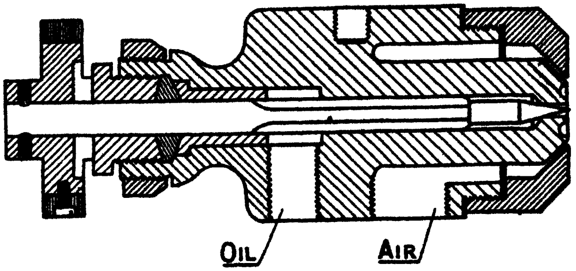


FIG. 25.—Urquhart's SFF Air or Steam Sprayer.

Clyde Low-pressure Sprayer. This works at an air pressure of only 3 to 14 inches water gauge. In Figure 26 the oil is regulated at the oil valve (2) and passing through the central concentric tube (6) is picked up by the air passing through tangential slots (7). The oil tube

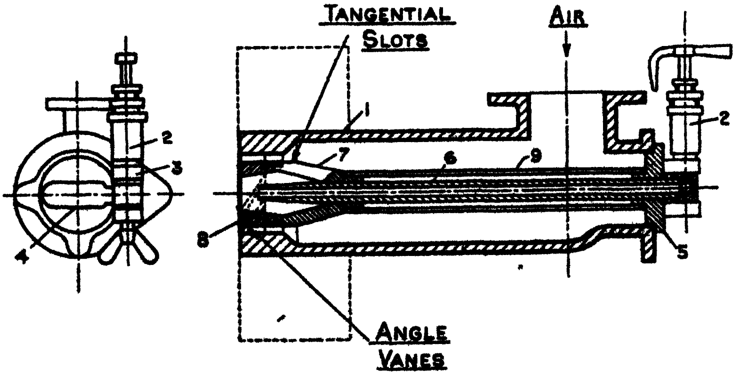


FIG. 26.—Clyde Low-Pressure Sprayer.

being of full bore right up to the end prevents choking due to carbonization.

Morgan Sprayer. For furnace work, particularly for metal melting, the Morgan Crucible Co. use a sprayer (Figure 27) which operates at a low air pressure, from 12 to 16 ounces per sq. inch at the burner, the air being supplied by a fan. Oil is drawn from an overhead tank through a pipe attached at (B) and passes through the oil tube (H) in the centre of which is the steel spindle rod (C) having a long tapered end. This serves to regulate the oil passing through the jet (J), the position of the rod being adjusted by the hand-wheel (D).

The air supply passes through the inner nozzle (F), this acting as the main atomizing air, and the outer nozzle (E), in both of which simply operated pressure adjustment is provided. With this dual adjustment it is claimed that when the oil being burnt is reduced to the minimum atomization is still perfect. About two-thirds of the air needed is supplied from the fan, the remainder being drawn in by the injector action.

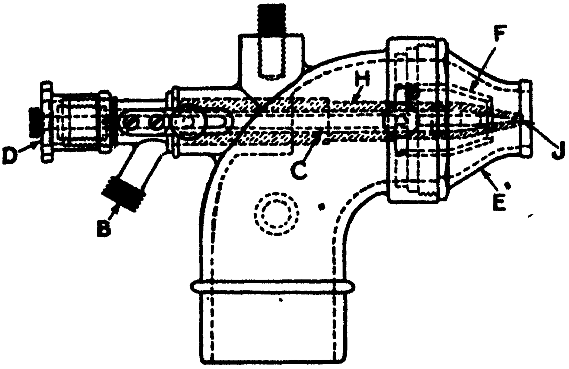


FIG. 27.—Morgan "L.S." Oil Sprayer (Air).

The Wallsend Low-pressure Air Sprayer (Figure 28). The air-pressure range suitable is from 8 to 20 in. water gauge. As will be seen from the sectional drawing (Figure 29) the internal parts are easily removed for cleaning. These burners have proved useful in auxiliary boilers in ships fitted with internal combustion engines, for small quantities of steam are frequently required.

The Wallsend-Howden Steam Jet Sprayer. For boiler use this may be employed where a pressure jet system is not advisable. The burner is mounted on the furnace front concentrically with an air distributor. As will be seen in Figure 29, there are two steam connections, the back one supplying the atomizing steam, and the other steam for blowing through the burner for cleaning, dismantling being unnecessary. The oil nozzle is designed to give a hollow conical spray, which the air passing between the vanes in the air distributor picks up forming a spiral flame.

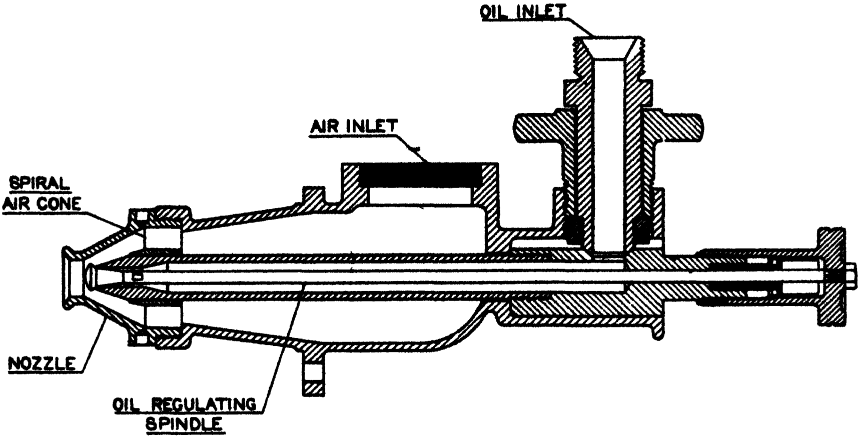


FIG. 28.—Wallsend Low-Pressure Air Sprayer.

Air required for Atomizing. In the United States trials (1902 Report) the average amount of air for 1 lb. of oil on 9 complete tests was 50 cu. ft., entailing an average consumption of steam (indirectly) of 0·4 lb., or 3·2 per cent. of the total steam generated. Analysis of the flue gases shows that very considerable excess of air was present, and the above amount is unnecessarily high. Other American tests on air sprayers showed that approximately 1 cu. ft. of air was required per lb. of steam raised. Assuming an evaporation of 13 lb. of water per lb. of oil, then 13 cu. ft. of air, or 1 lb., are required per lb. of oil.

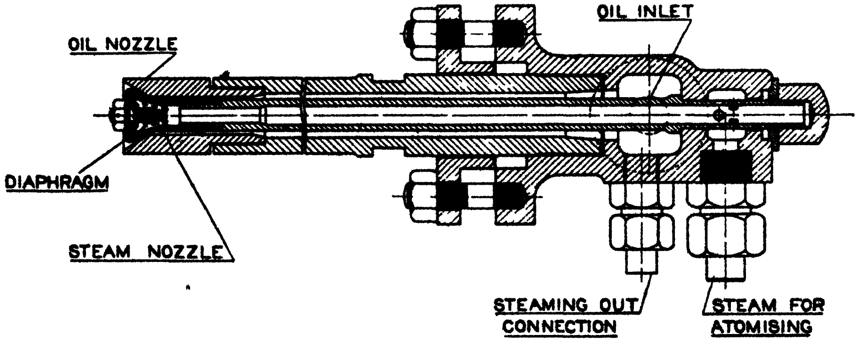


FIG. 29.—Wallsend Steam Jet Sprayer.

The pressure required for air atomizers varies greatly with the pattern. Kermode states that it need never exceed 3 lb. with his burners, and in a successful Russian installation the pressure is only $\frac{7}{10}$ths of an inch with the oil at 70° F. At a low pressure air is very economical, but as the steam consumption in compressors goes up rapidly as higher compressions are made, and the atomizing power of the air does not rise in anything like the same proportion, it will be seen that an atomizer requiring air at low pressure offers considerable advantage. With a good air atomizer the steam consumption should not exceed 1·5 to 2 per cent. of the total generated. The air for atomizing must not be confused with that required for complete combustion of the oil—it is usually less than one-tenth of the total air required.

Steam Consumption for Atomizing. Owing to the great variety of steam atomizers which have met with success in practice, the steam consumption for atomizing purposes, of which there are records, shows a wide divergence. It is indeed difficult to estimate the amount in ordinary practice where all the steam is from one boiler, and the most reliable figures are without doubt those of the United States Report on Liquid Fuel for Naval Purposes (1902). In these extensive and valuable tests a separate boiler was installed for supplying the atomizing steam, and on an average 0·6 lb. at 274 lb. pressure was required per lb. of oil. Allowing an evaporation of 13 lb. of water per lb. of oil, this is equivalent to 4·6 per cent. of the total steam generated. According to Bohler 0·85 lb. and to Grébel 0·80 lb. are required per lb. of oil. Much smaller quantities have been stated to have been utilized in some trials, but it is unlikely that over an extended period much less than 4 per cent. will be attained.

For heavy tar oils a greater quantity is required ; much will depend on the viscosity of the tar, and the temperature at which it comes in contact with the steam. Echinard, as the result of a large experience with French tars, gives the consumption as 1·5 lb. per lb. of tar, but this probably refers to practice with the thick carbon-laden tars produced in high-temperature distillation of the coal in thin layers. There seems to be no adequate reason why the more fluid tars from modern bulk distillation or low temperature carbonization should require appreciably more steam than a heavy oil residuum.

PRESSURE SPRAYERS

Primarily atomizers of this type are used for steam-raising.

As pointed out already, the oil spray is produced essentially by the mechanical breaking up of the issuing jet of oil, most commonly by imparting to it a high rotary motion. In earlier forms of atomizers, such as the Swensson, the oil jet was directed upon some type of baffle, but the objection to this method was the burning away of the protruding baffle. A recent form, the Rotamizer, relies upon a rotating cone throwing off the oil as spray.

Körting Sprayer. This was one of the very earliest sprayers in which the principle of breaking up the oil by imparting "spin" to the oil jet was used, and may be regarded as the progenitor of several of the modern pressure type sprayers. In this sprayer, which has been very successful in marine and other installations, the oil is forced through a channel in which a spindle having a deep thread cut out on the outside works, the coned part of the spindle opening or closing the small orifice through which the oil escapes from the nozzle. The hot oil, under pressure of at least 30 lb., thus has a sufficiently rapid rotary motion imparted to it to break up into a fine spray.

The Körting atomizer is illustrated in Figure 30, through the courtesy of the Editor of *Engineering*. Surrounding the atomizer chamber is an arrangement for the final filtration of the oil, which effectively prevents any clogging of the spraying device.

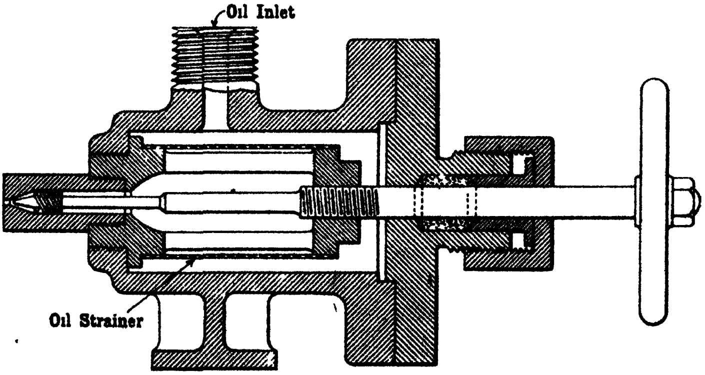


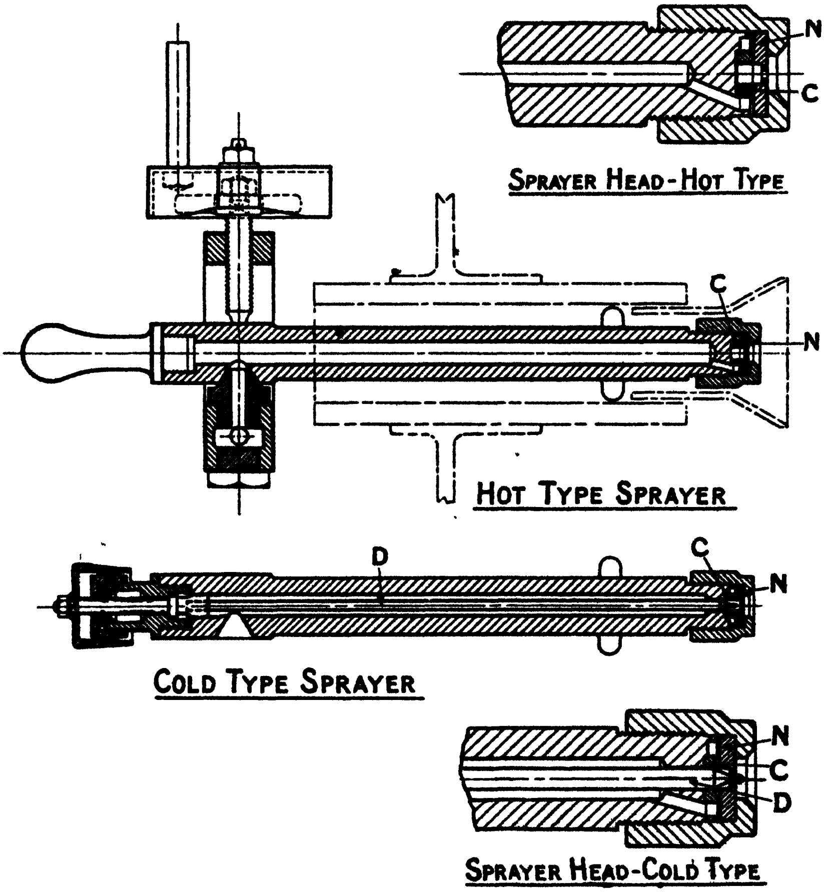
Fig. 30.—Körting Pressure Sprayer.

The White Sprayer. This pressure atomizer, made by Messrs. Samuel White & Co., of Cowes, introduces the novel feature in one pattern, the "hot or cold" type, of enabling cold oil of not too high viscosity to be fired, pending the heating up of the plant. The other or "hot" type works on the generally used principle of high centrifugal rotation imparted to the issuing jet.

In both patterns (Fig. 31) the oil passes through the tangentially arranged slots in the slot plate (C) to the centre chamber. In the "hot oil" type the oil channel is central to the longitudinal axis; in the "hot or cold" the centre consists of the sprayer spindle (D), the end of which passing through the orifice plate (N), terminates just outside. The specially shaped end of this spindle mechanically breaks up the issuing oil stream, to which a swirl has already been imparted.

Providing that the oil has a Redwood I viscosity not exceeding 900 seconds at air temperatures, steam may be raised from cold, but more viscous oils require heating.

Provision is made for withdrawing the spindle end inside the orifice plate by the handwheel at the front end, when the sprayer functions in a similar manner to the "hot" type. An illustration of the sprayer in action with cold oil is given (Fig. 32). From the clear appearance of the background it will be evident that the atomization is perfect.



SPRAYER HEAD-HOT TYPE

HOT TYPE SPRAYER

COLD TYPE SPRAYER

SPRAYER HEAD-COLD TYPE

Fig. 31.—White Pressure Sprayer.

Wallsend-Howden Sprayer. This sprayer (Fig. 33) consists of four parts, the body (A), the cap (B), a nozzle plate (C) through a central hole in which the oil jet finally issues, and the diaphragm (D) through which holes are drilled tangentially. The oil forced through the central

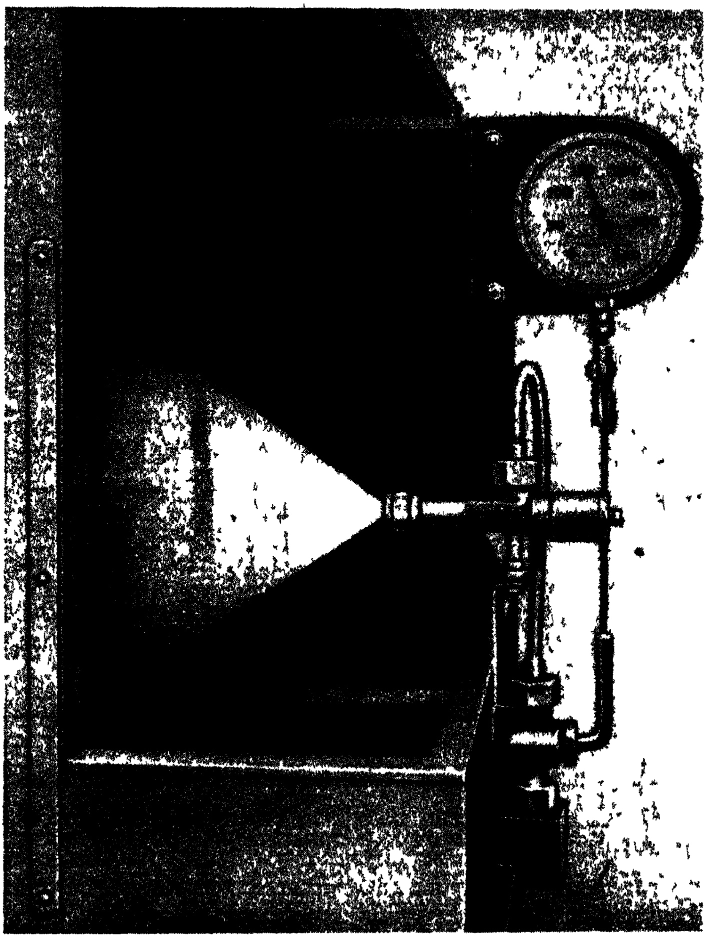


FIG. 32.—White Pressure Sprayer, Cold Oil.

channel passing through these tangential holes is given a powerful swirl which ensures it being ejected from the central hole in C as a fine cone of mist. A simple method is provided for the rapid dismounting and replacement of the atomizer.

Urquhart Sprayer. For this the special features claimed are that the throughput of oil is controllable without alteration of the oil pressure, which would require adjustment of the pumps; that oil can be circulated through the burner so that hot oil is available immediately on opening out, and that, through the central spindle being easily removable, clearing the jet is simple, but owing to the large nozzle this is required only at long intervals.

The regulation of the oil is made by alteration of the position of the threaded part of the central spindle (A) (Fig. 34), these threads being cut as a three start spiral, the depth increasing from nothing to a maximum along the length. The central spindle is moved by the hand wheel (B) working in a substantial square thread.

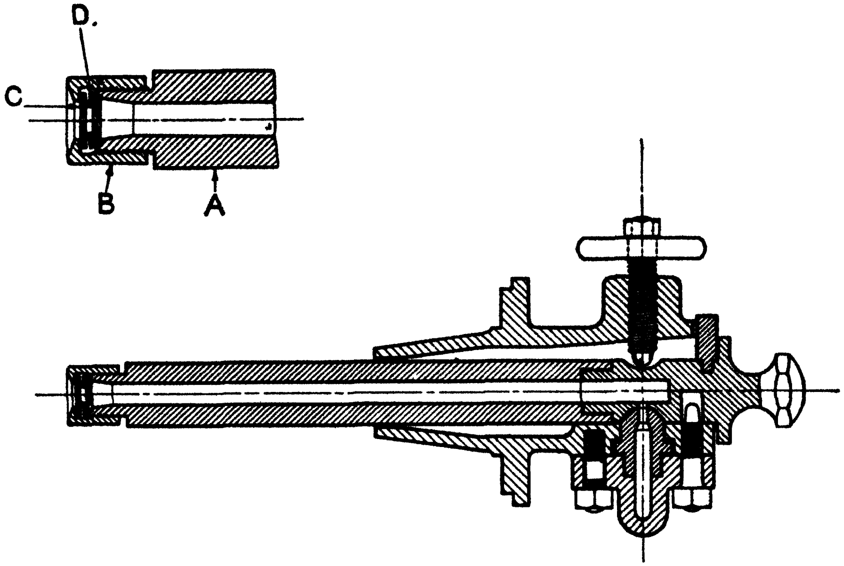


Fig. 33.—Wallsend-Howden Pressure Sprayer and Carrier.

The two channels for oil, supply and return, terminate in the circular chamber (D), which will be full of hot oil, easy to ignite when the burner is opened out.

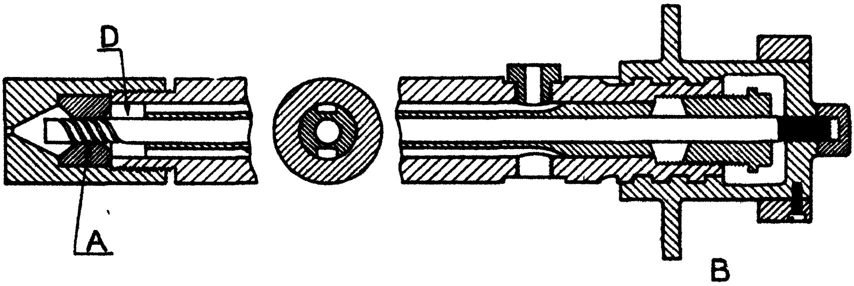


Fig. 34.—Urquhart Pressure Sprayer.

Clyde Sprayer. These have been fitted in a large number of ships, and it is claimed that their construction permits of efficient atomization from pressures of 25 lb. upwards, control being effected by adjustment of the oil pressure.

The oil is delivered through the central channel (A) (Fig. 35) and passes through four holes drilled through the diaphragm (B), on the front part of which there is a cone. These holes being drilled on a slope to the long axis, the oil reaching the chamber formed between the diaphragm (B) and the nozzle (C) is given a powerful swirl before escaping through the central hole in the nozzle.

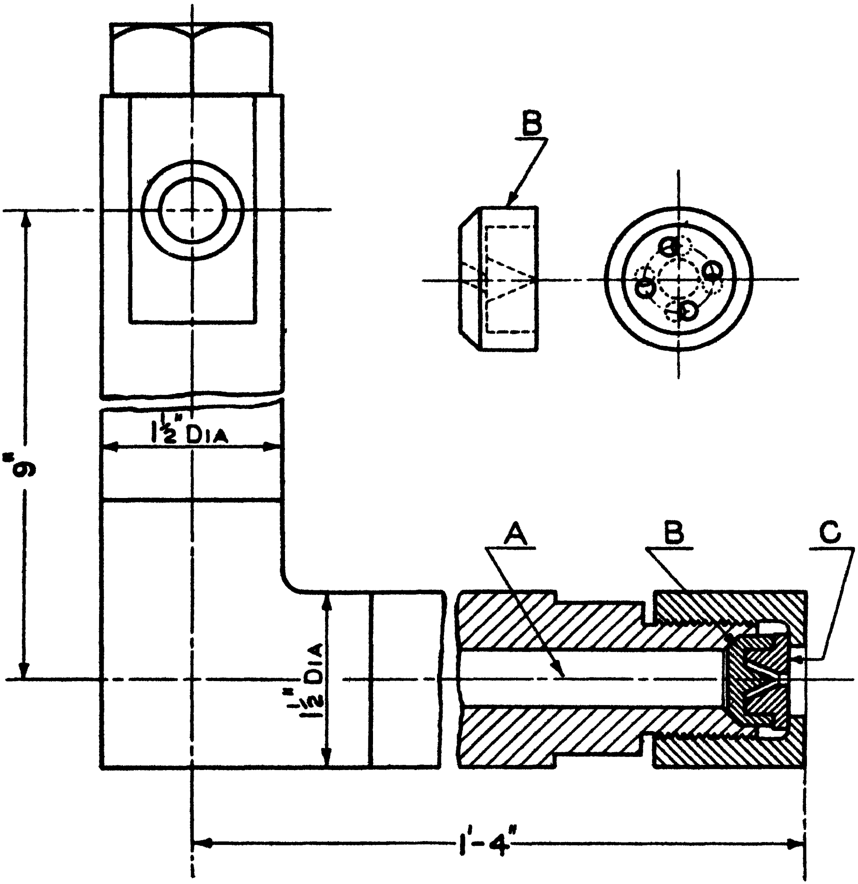


Fig. 35.—Clyde Pressure Atomizer.

Mechanical Sprayers

Oil fuel burners in this class are but little used for boiler firing, but are chiefly employed for furnace work.

The Brett Sprayer. The form of sprayer illustrated in Fig. 36 is one devised by the Brett Patent Lifter Co., of Coventry, for adaptation to any existing furnace. It will be noted that the oil jet, under low pressure, strikes against a rotating propeller (D) actuated by the air blast, and thus becomes broken up. By means of a baffle plate in the lower part of the vertical hollow column support (A), a portion of the air is sent round the space (B) surrounding the pre-combustion chamber (E), and in this way becomes highly heated before rejoining through the pipe (C) the other portion at a little distance below the slide valve shown. The position of the connecting pipes will be followed from Figure 38, which also shows how the waste heat from a pair of heating furnaces fired by this system is employed for raising steam in a water-tube boiler, an arrangement which frequently might be applied with other large oil fired furnaces.

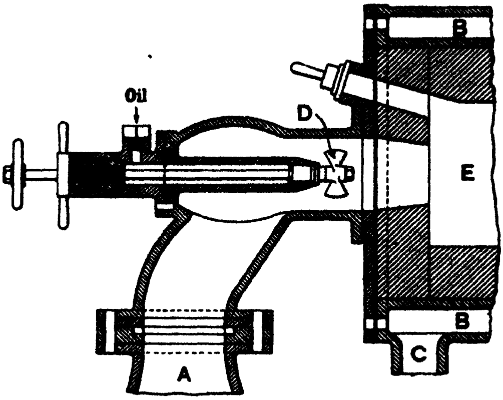


FIG. 36.—Brett Oil Sprayer.

The Rotamizer Sprayer. This is a good example of the centrifugal type. Air under a small pressure (7–12 in. water gauge) passes through the main trunk (A) (Fig. 37) and is controlled by the damper (B). It impinges tangentially on the rotor blades (C) which are mounted on the same hollow shaft as the atomizing cone (D), which will be revolved at a high speed. Oil fed through the central oil supply pipe to the cone is thrown off at the end as a fine mist by the centrifugal action, meeting with the air escaping around the cone. The rotating shaft carrying the vanes and cone is mounted on ball bearings.

An advantage claimed for this sprayer is that there is no possibility of choking, the full bore of the oil supply pipe being available, and in the smallest model this is not less than one-quarter of an inch diameter.

Domestic Heating. Many systems have been developed for using oil instead of solid fuels for heating the water circulated to radiators, etc., in large buildings. The use of oil eliminates ash and dust, the fuel space occupied is less, and delivery of oil to the service tanks is much simpler and cleaner than with solid fuels. Advantages in use include semi-automatic or completely automatic control; in the former the semi-automatic control involves temperature control by thermostats which determine fan speeds and oil consumption. In the fully automatically controlled plants starting up and completely shutting down, of the blower and burner and ignition must be provided for, also under thermostatic control. Ignition is usually arranged for by a high-

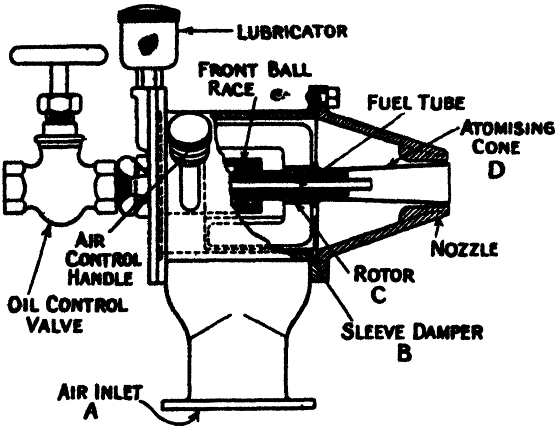


FIG. 37.—Rotamizer Sprayer.

tension spark, although in the Urquhart system low-tension (50 volts)' continuous or alternating current is used. Electric power is necessary for the blower, for any oil pump and for ignition. Low-pressure air burners are used.

As already mentioned, for these domestic plants special grades of fuel oil are usually employed and typical specifications will be found on page 152.

Comparison of Systems of Spraying. Each of the foregoing systems offers certain advantages, but on the whole the efficient spraying powers of the pressure burners, and the general convenience of their arrangement are in their favour, and certainly for steam-raising generally, but especially on board ship, this system offers so many advantages that it is superseding other systems. It is no secret that this is the system entirely employed in the Royal Navy and other navies, after exhaustive trials of the three.

Steam sprayers hold the advantage that the atomizing agent is always to hand in unlimited quantities and under good pressure when one boiler at least is working, and further, the space occupied is less than with the other systems. On the other hand, in starting up steam must be raised in one boiler of a set or in an auxiliary boiler with solid fuel. Further, all steam used in spraying is lost, and has to be replaced by feed water. This is of no moment in shore work, but on ship, where the supply has to be obtained by distillation, the loss of 4 to 5 per cent. at least of the steam is too serious a question.

According to the United States Report, steam sprayers do not lend themselves so readily to forcing as air sprayers.

Air sprayers are advantageous, first, in that the steam consump-

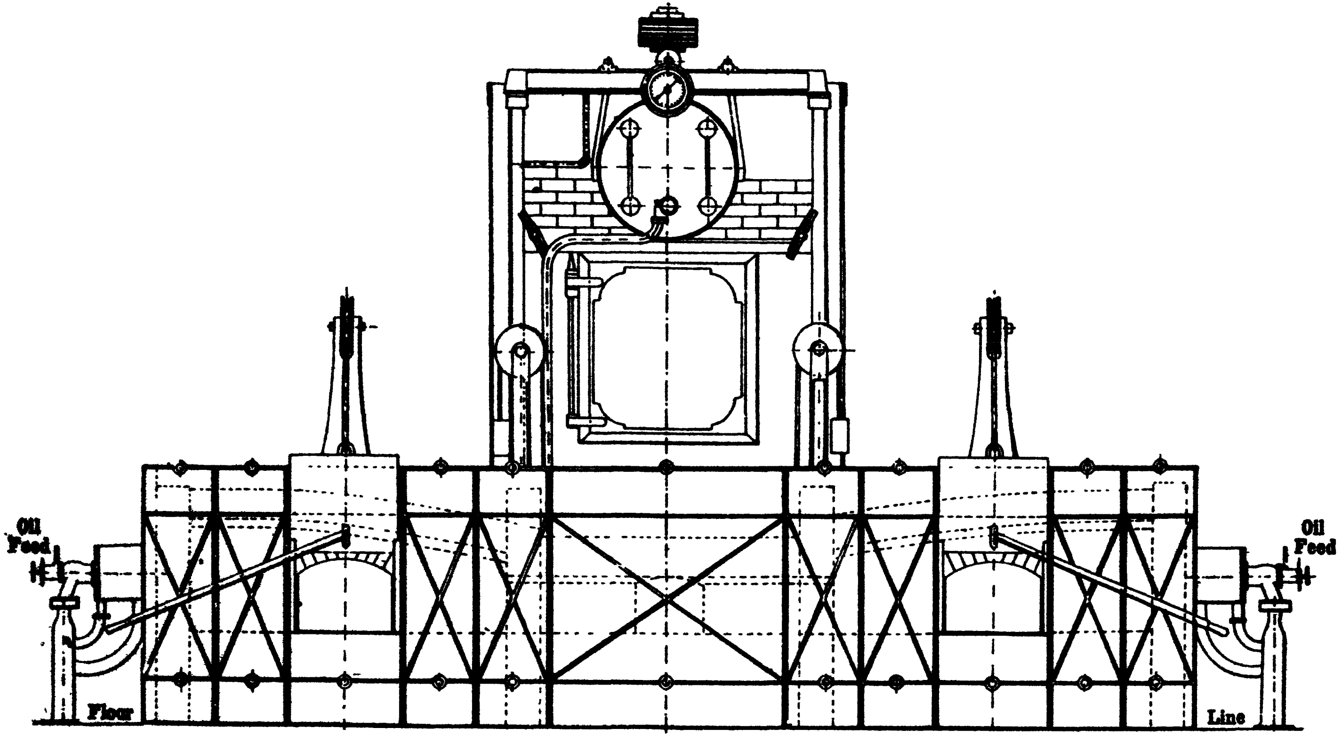


FIG. 38.—Arrangement of Heating Furnaces with Brett Sprayers with Babcock Boilers fired by Waste Heat.

tion for the compressor need be about only one-half of that for direct steam spraying, and, secondly, the whole of this steam may return to the boiler through the condensing plant. Air is the natural agent, since in the act of disintegrating the oil it must become properly mingled with the globules, ready to carry on the combustion. Steam, on the other hand, must displace a certain amount of air, and although extravagant claims have been made which postulate chemical interaction between the oil and steam which promotes the final combustion with air, results do not show any gain in efficiency. Any interaction between the steam and oil must be endothermic (absorb heat), and this, together with the displacement of air by steam, will extend the zone of combustion farther into the furnace. The claim often made in the past that steam actually promoted the combustion of oil in the furnace is difficult to reconcile with the fact that outside the furnace it is one of the most effective agents in extinguishing an oil fire.

For metallurgical work, glass furnaces and other industrial operations, air injection is the most applicable system.

The space occupied by suitable compressors, especially those of the rotary type, is not great, and a small internal combustion engine or electric motor can be used for the drive.

With the pressure jet system very perfect disintegration may be effected, and no difficulty is experienced in getting perfect air admixture. On board ship the pumps for the burning system must be entirely separate from other pumps. It is more particularly in competition with steam atomization in boiler practice, and here there is no question as to the great superiority of the pressure system.

With both air and pressure systems, starting can be arranged for hand, motor, or internal combustion engine driven pumps or compressors.

Combustion of Oil Fuel. Special consideration has to be given to the furnace arrangements for the combustion of oil fuel for steam-raising. Little difficulty is experienced in obtaining perfect combustion and high efficiency where the duty of the boiler is low, but it is otherwise when a high duty is demanded and a large quantity of oil has to be consumed. It is for this reason that the solution of the problem of the smokeless combustion of oil fuel was established at a much earlier date in the mercantile marine and in shore practice than under the conditions existing in a warship.

The conditions for perfect combustion differ radically from those existing in the case of solid fuel. When coal is burned beneath a boiler, by destructive distillation some 11,000 to 12,000 cu. ft. of gas, as measured at ordinary temperatures, and about 10 gallons of tar in the form of vapour are evolved per ton, whilst 75 per cent. of the coal is burnt as solid fuel on the grate, and the relationship between heating surface and grate area is of importance.

In the case of oil, practically the whole is burnt as gas or heavy vapour, and considerations of grate area are quite irrelevant; the essential factor is cubic feet of combustion space.

Not only is the question of generous provision of combustion space indicated by the above considerations, but also by reason of the greater amount of air theoretically demanded per lb. of oil fuel as compared with coal. Taking average compositions for the two classes of fuel, the following comparison between the theoretical air supply is possible :

	Weight of air per lb.	Volume of air in cubic feet	
		at 0° C.	at 60° F.
Coal	11·5	140	147
Oil	14·0	172	181

In the series of American trials, in endurance tests of 116 hours' duration and a combustion space of 121 cu. ft., the following relative results for coal and oil (air-injection) were obtained :

	Natural draught.		Forced draught.		
	Lb. per cu. ft.	Evaporation from and at 212° F.	Pressure inches.	Lb. per cu. ft.	Evaporation from and at 212° F.
		lb.			lb.
Coal	8·3	10,000–11,000	3·00	30	30,150
Oil	7·6	15,000–16,000	3·75	27	35,560

The guiding principles for the ensuring of complete combustion and absence of smoke have been laid down already, namely, sufficient air, proper admixture and maintenance of temperature.

The air supply in the case of oil fuel may be divided into *primary air*, the injection air where this system is used, or air drawn in by the injector action of the atomizer, and *secondary air*, or air supplied to complete the combustion partially carried out by the primary air or of any oil spray or vapour not yet attacked. For smokeless combustion not only must the air supply be efficient, but it must be mingled as intimately as possible with the escaping spray, and there must be no local cooling. Primary air does not need heating, as combustion in the region of its action will always be sufficiently vigorous to maintain a high temperature, but when special provision is made for secondary air to be introduced, such air is best supplied at as high a temperature as possible. There is no tendency for smoke production during the first 18 in. or 2 ft. of the flame; smoke is produced by the less rapidly moving portions constituting the farther end of the flame. Here it is that the proper admixture of hot secondary air is best arranged for. Attention may be again directed to the case of the oil lamp flame with and without the chimney (p. 97).

The United States Navy Fuel Board laid down the following as the essential conditions for the production of a short hot flame: the fuel should be a pure carbon-hydrogen oil, there should be initial heating of the air, intimate diffusion of the fuel and air, and a large surface of fuel exposed to the impact of the air.

Suitable arrangement of firebrick plays an important part in the successful combustion of oil fuel in many installations. In water-tube boilers, where there is ample space between the banks of tubes on either side, or where the lower rows are situated fairly high above the combustion space, the burners may play directly into the space. Where, however, there is any risk of flame impinging directly on the tubes, these should be protected by firebrick; the bottom and sides will be necessarily of firebrick. Suitable firebrick arches and baffles, however, are in many cases essential to success, for they may perform several important functions; heavier particles of oil falling on them are vaporized; they form efficient radiating surfaces (the inefficiency of flames in this respect has been pointed out already); lastly, properly arranged baffles prevent long tailing flames where combustion is often incomplete, and smoke forms by reason of the difficulty of mixing the air properly without some such arrangement. These baffles serve the purpose of admixture, and they maintain the high temperature at just the point in the system where checked combustion, with smoke formation, would otherwise probably result. Further, they may be

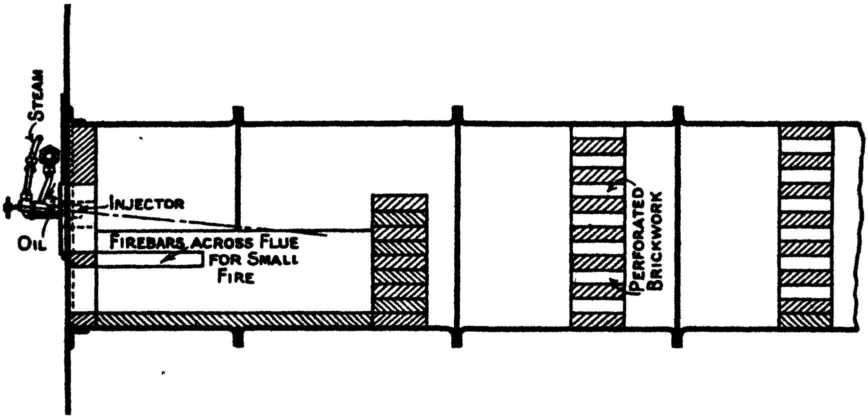


Fig. 39.—Furnace Arrangement in Lancashire Boiler.

easily constructed to enable the highly heated secondary air to be introduced effectively just where most required.

As an illustration of the use of firebrick arches and baffles the Holden design for a Lancashire boiler may be considered (Fig. 39) It will be seen that the hot gases and air at the outer end of the flame first strike a chequer work of firebrick extending half-way up the furnace; they are further thoroughly mixed by the two succeeding baffles, which extend completely through the combustion space. A short "grate" of firebrick extends immediately beneath the burners and serves for lighting up, and when fairly running would vaporize any heavier oil particles which might settle, although this is not a likely occurrence with such efficient atomizers.

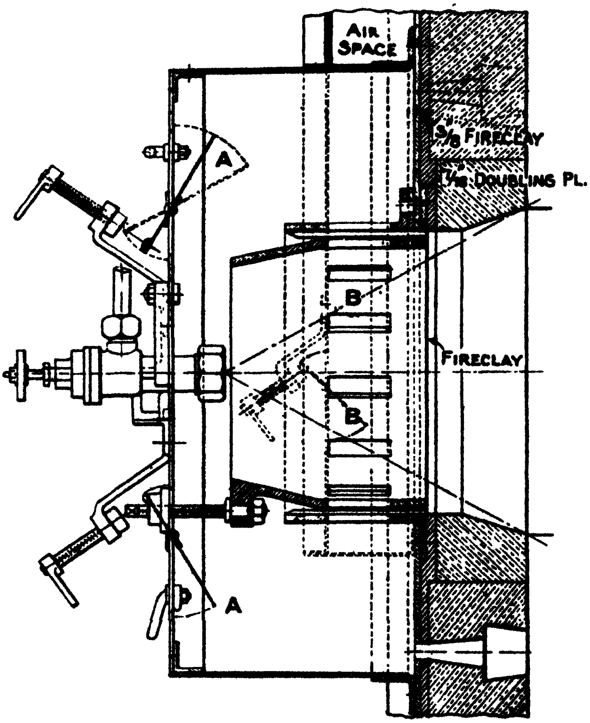


FIG. 40.—Furnace Front for Fuel Oil.

With water-tube boilers, especially for marine use, it is general practice to fit an extension to the furnace, at the outer face of this the sprayer is mounted, and the air supply is directed through an inner ring with a series of openings fitted with deflecting plates so that the air is given a powerful swirling motion, thus ensuring its proper mixing with the oil spray. The arrangement used by Kermode is illustrated in Figure 40; the air is first passed through the adjustable openings

(A) in the outer plate into the circular chamber, whence a portion passes through the inner ring of openings (B).

Liquid Fuel for other Purposes than Steam-raising. Liquid fuel has been employed most successfully for a large number of industrial operations, amongst which may be mentioned melting metal for casting, etc., in glazing kilns, muffles for enamel ware, rivet heating, glass melting and annealing. Not only has it been employed where high temperatures are desired, but, since the temperature attained is so well under control, it has been used successfully for the delicate operation of tea-drying and for drying bagasse preparatory to its use for animal foods.

The high intensity which is attainable, the ease of control of the temperature, the absence of ash and, with good oils, of more than traces of sulphur, render it particularly suitable for many metallurgical operations. Further, once the proper adjustment of air supply has been made, the nature of the combustion is constant, there being no opening and closing of fire-doors admitting varying quantities of air. In all such applications the conditions of use are far more favourable to perfect combustion than in steam-raising, since the temperature of the furnace or material generally is not greatly removed from the flame temperature. For good results firebrick should not be spared. There appears good reason to believe that hot surfaces of firebrick act catalytically in promoting combustion. Heavier oil particles are gasified readily, and the atomization need not be nearly as perfect as for boiler work. A simple type of burner in which a regular drip of oil is picked up by an air blast is frequently sufficient, and low air pressure is all that is required if a good type of burner is employed.

The air seldom requires pre-heating for metallurgical furnaces. In many cases it is advisable to instal a pre-combustion chamber as an extension of the furnace; into this the burner is directed, and combustion partially carried out by the air used for injection. Secondary air should be supplied around the junction of the pre-combustion chamber and the main furnace.

Furnaces of the reverberatory type may be arranged easily for oil-firing, and although the system is not so generally advantageous for metallurgical purposes in comparison with producer gas with regeneration, tank furnaces of a similar type for glass melting have been in continuous successful operation for periods of over two years without the burners being turned off. The temperature required is about 1500° C. (2730° F.).

The output is greatly increased, considerable economy in space is effected, and more men can be employed working the glass at each furnace.

Metallurgical operations in which oil fuel is employed for melting purposes are conducted usually in tilting furnaces of the Bessemer type, in which the oil is sent directly into the furnace, or in crucible furnaces of a tilting pattern, the crucible being fixed in a fireclay-lined furnace mounted on trunnions. This system has many advantages (equally true when gas-fired) in that lifting the pots, with consequent liability to fracture and loss of metal, is avoided, larger pots and greater charges may be employed, and consequently considerable saving on fuels is possible. Detailed description of such furnaces is outside the scope of the present work, but one or two typical examples are illustrated.

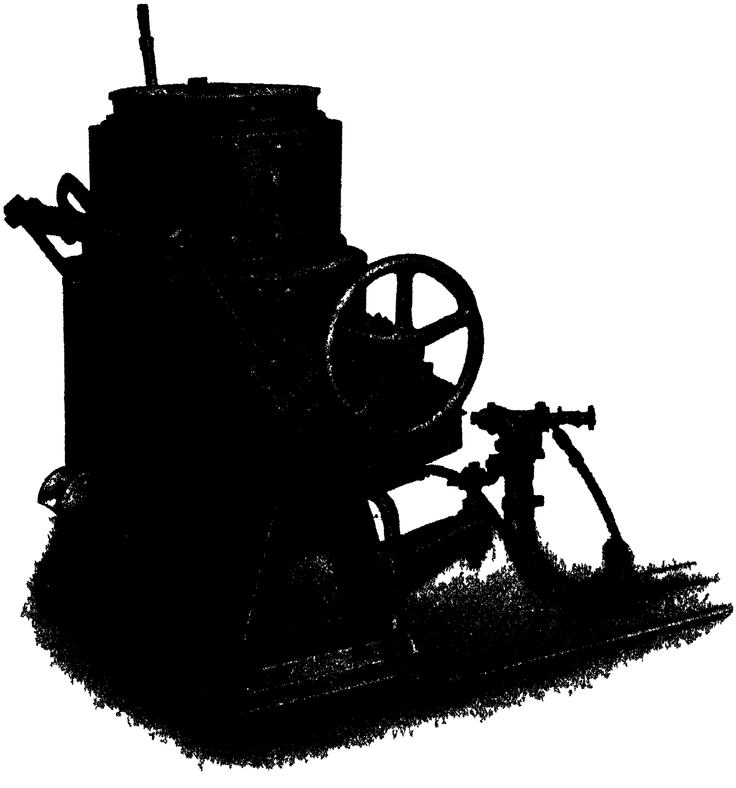


FIG. 41.—Morgan Furnace.

For metal melting, where it is important to keep the metal from contact with the atmosphere of the furnace, the crucible type is employed; in other cases the flame may play directly into the melting chamber.

The smaller-sized crucible furnaces usually have the tilting trunnions on the axis passing through the centre, and the charge is teemed into ladles for conveyance to the moulds. Larger furnaces for direct pouring may have the trunnions arranged in front of the furnace, in line with the pouring spout, counterweight gear being provided.

Another type which permits of the body containing the melt being lifted out from the cradle by a crane and moved by overhead gear to the moulds and there tilted in the usual manner is illustrated in Figures 41 and 42.

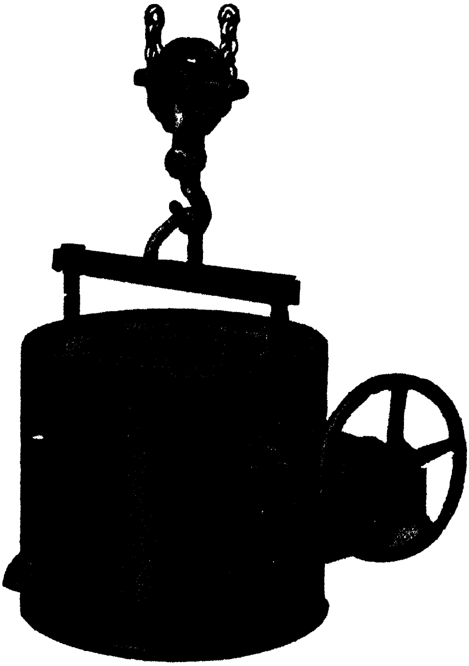


Fig. 42.—Morgan Furnace.

Some results obtained with oil-fired tilting furnaces are given in Table XXXVI.

TABLE XXXVI

Metal Melting in Oil-Fired Tilting Furnaces

	Brass.		Bronze.		Aluminium.	
Weight of charge (lb.)	250	1120	250	1120	80	375
Average time of melt (min.)						
First heat	55	100	60	110	35	60
Other heats	35	70	40	75	20	35
Total weight of metal melted in eight hours (lb.)	2250	6720	2000	5600	1040	3375
Oil used per 100 lb. of metal (lb.)	12	8	13	9	16	12

The furnaces used for aluminium were of the same size as used for the brass melting, but owing to the much lower density of the metal the full charge was roughly one-third.

ECONOMIC ASPECTS OF LIQUID FUEL

The practical advantages which liquid fuel possesses as compared with coal when consumed under boilers have already been dealt with, but they will be summarized briefly here as greater evaporative power, ease of handling, cleanliness, absence of ash, clinker, etc., combustion with little attention once the proper conditions have been arrived at, all leading to appreciable saving in the costs of operating a plant either for power or general industrial purposes. Further, the very great success which has attended the introduction of heavy oil engines of the compression-ignition type, for general power purposes, and particularly the high-speed engines of this type, now widely used in road and rail transport services, has added to the importance of the question, and renders it essential that careful consideration should be given to the economic aspects of the supply of liquid fuel. More especially is this the case in countries where petroleum oils, which furnish by far the largest proportion of liquid fuels of a suitable character, must always be imported fuels, and therefore dependent largely upon conditions outside our control.

Supplies. The output of oil from the various oilfields of the world is given in Table IV, Appendix. In little over two decades (1912–33) the world output has become nearly four times greater, being little short of 200 million metric tons, a figure approaching the British coal output to-day, yet a fraction only of the world output of coal. For a proper comparison of the coal output with the total oil production of the world, the relative value of oil as fuel in terms of coal must be taken. In the case of steam-raising, allowing for all the economies of oil, its superior evaporative duty and other advantages, it may be taken that 1 lb. of oil is equivalent to 1·5 lb. of coal. In internal combustion engines using heavy oil, the type which gives the highest efficiency, it will be approximately correct to take the consumption per B.H.P. as 0·5 lb. with regular running conditions, as against an average consumption of 2 lb. per B.H.P. Oil then may be converted into terms of coal in the two cases respectively by the factors 1·5 and 4.

According to figures issued by the Board of Trade, the fuel oil (including bunkers and Diesel oils) retained for home consumption in 1932 was 405 million gallons and to this must be added 153·3 million gallons from crude oil refined in the country—so that the total approximate consumption of fuel oil of all classes was 558·3 million gallons. Allowing 240 gallons of fuel oil to the ton and the coal equivalent to oil as 1·5,[1] this quantity of oil amounts in terms of coal to some 3,450,000 tons. The coal actually used for industrial purposes in 1932 was estimated at 114·5 million tons.

It is clear that, great as are the advantages that liquid fuel undoubtedly possesses, and with the great advances in output of the last few years, it is still a fuel of secondary importance for steam raising and heating purposes in general, but in countries where it is bountifully supplied by nature, the enormous quantities there available render it the fuel demanding pride of place. The question of its general use resolves itself entirely into a question of locality, for an imported fuel is never likely to supersede a fuel native to the country or district, except for special applications where its practical advantages outweigh the disadvantage of its foreign source.

The point is well illustrated in the case of the Mexican Railways. At one time from 120,000 to 140,000 tons of patent fuel were imported from South Wales for locomotive use. To-day oil has supplanted solid fuel.

For certain special purposes, such as for steam-raising on board ship, the advantages of liquid fuel place it far above coal as a fuel, and many of the largest liners have been converted from coal to oil, but in this country no large extension of the use of oil fuel for other purposes has taken place.

The development in the use of heavy-oil engines has been rapid and is ever increasing. Many large motor-ships have been added to the mercantile marine in recent years. The provision of suitable fuel for such engines is a vital problem, and petroleum products are unrivalled. So far the industry has been able to meet all demands owing to the big increase in oil production.

Great fluctuations in supplies and prices of liquid fuel have arisen in the past; the possibilities of interference with transport either through a series of accidental causes, or in the event of war, must always place an imported fuel at a serious disadvantage with a native fuel. Recognizing all the great advantages which it possesses, advantages which in spite of possible uncertainty of adequate supplies are bound to lead to its far greater employment in the future, it becomes necessary to consider what sources of such fuel are open in this country.

Shale oil has been shown to be almost identical in character to the natural petroleum oils, and the heavier distillates are amongst the finest fuel oils. For many years about 3,000,000 tons of shale were retorted in Scotland and from the products about 150,000 tons of high-grade fuel oil were obtained. Production fell to just over 2,000,000 tons in 1930 and in 1932 to below 1,400,000 tons, so that supplies from this source are very small in comparison even with the present demand. Large quantities of shale oil will become available in New South Wales and New Zealand when the deposits there are worked on an extensive scale.

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[1] For compression-ignition engines a coal equivalent of 4 : 1 should be taken, but no data is available as to the relative amount of oil used "free" and in compression-ignition engines.

The tars obtained from coal gas and coke-oven plants are certainly the most promising source of supply indigenous to Great Britain, and, with still wider use of liquid fuel, a very extended use of such products as the raw material must follow in all countries where oil is not the native fuel.

It is difficult to compute the annual production of tar from these two sources: under normal conditions about 17,500,000 tons of coal are carbonized annually in the gasworks, and about 20,000,000 tons in coke-oven plant, but in many cases no tar recovery is made. From the returns of 1931–1932 a little over 210 million gallons of tar were produced by statutory undertakings, and according to recent reports (Alkali Inspectors' Reports) about 1,600,000 tons of tar are " treated " annually in Great Britain and Scotland.

Crude tar (not containing any quantity of free carbon and fairly free from water) has proved a success for steam-raising, retort-heating, etc., but a very material change has taken place in the position of tar as a fuel since about the year 1909, when a marked advance in price set in. Several causes contributed to this, notably the increased use of tar for road spraying, the increased value of pitch, used for briquetting coal, and the good prices obtained for benzole and creosote oils.

The natural effect of this rise has been shown by the practical discontinuance of the use of tar as fuel at gasworks and on the Great Eastern Railway, where at one time a large number of locomotives were running wholly or partly on tar oils.

For Diesel-type engines in this country the use of tar oils was made compulsory during the Great War, because of the great demand for fuel oil for naval purposes, but to-day they are seldom employed.

Much attention has been paid to fuel oil production from the low-temperature distillation of coals, and of otherwise low-grade or waste bituminous substances. Low-temperature distillation processes and products have been discussed earlier (p. 140). By such methods no doubt considerable quantities of fuel oil, of moderate quality as compared with petroleum products, could be obtained, and as there would be the advantage if coal were used of producing a smokeless fuel such schemes have found enthusiastic advocates on the ground of the abatement of the smoke nuisance. The possibilities are discussed in the Fuel Research Board Report, 1918–19, to the following effect—that as only 5 to 8 per cent. of the coal could be obtained as fuel oil, every million tons of oil from this source would involve the diversion of 15–20 million tons of coal from other channels of consumption, and suitable markets for the 65–70 per cent. of coke would have to be found.

According to an official statement, 1 ton of coal produces 14 cwt. of semi-coke and 16 gallons of tar, which in turn yields from 5 to 8 gallons of fuel oil. If the whole of the 35 million tons of domestic coal were treated (an obviously impossible proposition) the yield of fuel oil would approximate to one million tons per annum. The Secretary for Mines stated (1934) that nine low-temperature carbonizing plants were in operation and that in 1932 318,000 tons of coal were carbonized.

The demands for the more volatile fuels for engines for the vast number of road vehicles and for aviation has become prodigious, the consumption of motor spirit in Great Britain now amounting to over 1000 million gallons—rather more than half the total home consumption of petroleum products.

It is evident that although fortunately there has been a continual increase in the petroleum production, the demand for petrol in most countries, including a great producer like the United States, is an ever-increasing one. When it is considered that the increase in the production of oil must cease; that no augmentation of supply is taking place through present natural production; that the development of the petrol engine in oil-producing countries leads to big demands for home-produced petrol, it is evident that alternative fuels must be considered, unless the use of such engines is to be hampered seriously, with a corresponding check to a big branch of engineering.

The alternatives appear to be:

1. The use of petrol boiling over a wider range, or mixtures of petrol with a certain proportion of illuminating oils.

2. Supplementing supplies from (*a*) cracking processes, (*b*) natural gas condensates, etc.

3. The extended use of fuels from sources other than petroleum, e.g. benzole and alcohol.

4. The hydrogenation of coal and coal tars.

Limitations are imposed on adopting the first alternative because of the impossibility of burning completely hydrocarbons boiling above (approximately) 200° C.

Cracking processes have been largely extended, with the dual objects of increasing the yield from crude oils and the production of motor spirit of high anti-knock value, and recovery from natural gas (and to a less extent from uncondensed still gases) has been materially expanded. The last returns available show that of the total motor spirit produced in the United States 48 per cent. was "straight" spirit; 44·5 per cent. from cracking processes and 7·5 per cent. by condensation of natural gas.

The use of benzole and alcohol as alternative fuels is of great importance. The former is a home product and, as shown previously, eminently suitable for use in petrol motors. The latter, although its production on a large scale in this country is unlikely to enter into serious competition with the production in many of our Colonies, may be regarded in any case as a possible fuel of entirely British production the raw material for which is available in large amounts.

Motor benzole production 1929–33 averaged about 30 million gallons per annum, but with the advantage of the duty on imported motor fuels, from which home products are exempt, encouragement to extend recovery from coal-gas and coke-oven plants is increasing production materially. Actually, owing to war conditions, recovery of benzole and toluole was made compulsory, and in 1918 10 million gallons of benzole were obtained in the gasworks and 32 million gallons in coke-oven plants, but the latter were then at a peak of production.

By the low-temperature carbonization of 318,000 tons of coal in 1932, 741,000 gallons of "motor spirit" were obtained.

Alcohol for fuel purposes is, at present, available in such limited quantities that its use is mainly restricted to special mixtures (p. 242) used principally for racing.

The use of alcohol as a fuel in this country was almost impracticable a few years ago because of the Excise restrictions. Considerable relaxation of these in relation to alcohol for power purposes has been made, and "power alcohol" can now be handled and marketed in bulk (p. 236), but there must be always less freedom of action because of necessary Excise restrictions than with the other high vapour-pressure liquid fuels. A really satisfactory denaturant is essential to further relaxation of the regulations.

The advantages of a fuel derived from home-grown products, or possibly from raw materials produced at a lower rate in the Colonies, are apparent. Its adoption certainly would give encouragement to agriculture; it would provide a national weapon to fight artificial (or economic) shortage of other fuel for internal combustion engines; indirectly it would encourage the further development of a big and growing branch of engineering, the success of which is impossible without an assured supply of fuel at a reasonable cost. From every point of view it would appear that the claims of alcohol as a fuel are now so insistent that they can hardly be ignored.

Whilst alcohol alone can be regarded only as a useful auxiliary supply of motor fuel, its use in admixture with benzole is developing considerably.

Motor spirit obtained from coal by hydrogenation has been proved a technical success; and also by hydrogenation of tars and heavy asphaltic petroleum oils. The latter present less practical difficulties than the direct treatment of the coal. In Germany large quantities of spirit have been produced from brown coal and from tars and in this country an extensive plant, in course of erection, will furnish later data from which the process may be judged from the point of view of its commercial aspects.

The fact cannot be overlooked that from the point of view of fuel economy and the conservation of our limited (but admittedly considerable) coal reserves the production of light motor fuels from solid coal is indefensible whilst abundance of material can be obtained much cheaper from the vast petroleum resources of the world.

In considering the present increasing use of these fuels of high vapour pressure cognizance must be taken of the influence of the modern high-speed compression-ignition engine, using fuels of low vapour pressure. Already these engines are in wide use for the heavier types of road vehicles and to a small extent for aviation, and there can be no doubt that an increasing proportion of transport will be operated by heavy oil—indeed some authorities have predicted an almost complete substitution of petrol as fuel.

CHAPTER X

PETROL OR GASOLINE

In the early days of the motor industry petrol was obtained entirely by the distillation of crude petroleums, the naphtha fraction being redistilled to give the desired range of distillation of the final product. Refining by acid and soda washing removed any small amounts of unsaturated hydrocarbons, traces of colour, etc. Modern refineries carry out the distillation of the crude oil in tube stills, with "bubble columns" (p. 158). Such petrol is known as "straight spirit."

With the ever-increasing demand for motor spirit for use in cars and aeroplanes it became necessary to increase the yield obtainable from crude oil, and this led to the extensive introduction of "cracking" processes. Prior to this on an average the "straight spirit" produced amounted to only some 12 per cent. of the total crude oil treated. By cracking this has been raised to over 40 per cent.

A further source of supply has been from the vast quantities of "natural gas," which by suitable recovery processes yields petrol, or natural gas gasoline, of high volatility and purity. Only about half the U.S.A. production of motor spirit to-day is "straight spirit," over 40 per cent. is cracked spirit and less than 10 per cent. is obtained from natural gas.

Cracked Spirit. Details of production cannot here be entered into, but the general principle of the cracking process is to subject the higher boiling fractions of the crude oil, and in some cases suitable crude oil itself, to such a high temperature that the complex heavy molecules are broken down, with the production of much gas, some free carbon, heavy residues which have resisted decomposition or have formed in the process, and low-boiling hydrocarbons which constitute the raw "cracked spirit."

Several factors determine the character of the product. Cracking may be carried out in the "liquid" or "vapour" phase. The pressure employed is usually high, and has great influence on the composition of the product; temperature is, of course, a most important factor and, in addition, the character of the cracking stock will determine the best conditions of treatment. In most plants the cracking stock is an intermediate oil such as the gas oil fraction.

Modified cracking processes are used also to improve the engine characteristics of already produced spirit, "re-forming."

To reduce the quantity of unsaturated hydrocarbons many processes involving " hydrogenation " in the presence of a suitable catalyst have been devised, but little cracked spirit of this type is actually produced from petroleum.

" Natural Gas Gasoline " (or Casing Head Spirit). As already mentioned, nearly 10 per cent. of the American petrol production is from natural gas. Much of the natural gas produced is known as " dry gas," and consists almost entirely of the first two or three members of the paraffin series of hydrocarbons. " Wet gas " derives its name from the condensation by cooling and pressure of small quantities of higher members of the series. It is this type which is treated for the production of the " natural gas gasoline." The physical constants for the lower members of the paraffin series are given in Table XXXIV.

TABLE XXXVII

PARAFFIN HYDROCARBONS

	Boiling point deg. C.	Critical temp. deg. C.	Critical press. atmos.
Methane	− 164	− 95·5	50
Ethane.	− 84	+ 34	50
Propane	− 44	97	44
Butane (normal)	+ 0·3	—	—
„ (tri-methyl-methane	− 17	—	—
Pentane (normal)	+ 36	197	33
„ (iso-)	30	194	33
Hexane (normal)	69	250	30

Methane and ethane, the two chief hydrocarbons present, do not readily liquefy, indeed, if liquefied, their high vapour pressure precludes their being retained in a liquid condition, but the boiling point of the immediately succeeding members of the series enables practical use to be made of these in the liquid form.

Three methods are employed for obtaining the liquid product: (1) by compression (generally in stages) and cooling, (2) by oil scrubbing, (3) by absorption, usually with active carbon.

In the first method liquefaction by stages may be conducted to yield (*a*) a stable yet highly volatile spirit, (*b*) a second product of such high volatility that alone it is not of use, but which can be profitably employed by blending with fairly heavy naphthas, (*c*) a still more volatile product, largely composed of butane and pentane, which can only be retained in liquefied form under pressure. It is marketed in cylinders, in a similar way to ammonia and carbon dioxide. This liquid " gasöl " or " liquid gas " is of very high calorific value, averaging 2400 B.Th.U. per cu. ft.

The petrol obtained from the oil or charcoal absorption, being in either case driven off by heat and condensed, yields directly a stable product. These two processes are superseding the compression method

—they are more economical and natural gases containing lower amounts of liquefiable components can be economically treated.

H. C. Allen (*Ind. Eng. Chem.* (*Anal.*), 1929, **1**, 226) gives the following details for a rich casing head gas, yielding 2·2 gallons of petrol per 1000 cu. ft.:

	Untreated gas. Per cent.	Treated gas. Per cent.
Methane	41·4	46·1
Ethane	24·4	28·7
Propane	16·7	15·5
Butane	6·8	4·3
Pentane	4·9	0·2
Hexane	1·2	trace
B.Th.U. per cu. ft.	1755	1509

Natural gas spirit is not used alone but is usually blended with "straight spirit," alternately with heavy naphthas, those just outside the normal range of distillation of petrol, thus rendering a wider range from a crude oil available as a motor spirit.

Uncondensed gases from stills and cracking plants are also profitably treated in modern refineries for the recovery of the low-boiling liquid hydrocarbons.

Composition of Petrols. Straight petrol is a mixture of a large number of hydrocarbons of various series. It consists mainly of the lower liquid members of the paraffin series and of "naphthenes," together with small amounts of the benzene series of hydrocarbons. Since the spirits have been treated with sulphuric acid for purifying purposes it is improbable that unsaturated hydrocarbons are present to any extent.

Usually petrol distils completely between 40° and 200° C., and the principal normal hydrocarbons falling in this range may be:

"Normal" Paraffin Hydrocarbons

	Formula.	Boiling-point ° C.	Specific gravity D^{20}_{4}	Specific heat.	Latent heat of vaporization.
Pentane	C_5H_{12}	37	0·63	—	—
Hexane	C_6H_{14}	69	0·66	0·527	79·4
Heptane	C_7H_{16}	98	0·68	0·507	76·5
Octane	C_8H_{18}	125	0·71	0·505	71·0
Nonane	C_9H_{20}	150	0·72	0·503	—

"Naphthene" Hydrocarbons

	Formula.	Boiling-point ° C.	Specific gravity at 0° C.	Specific heat.	Latent heat of vaporisation.
Pentamethylene	C_5H_{10}	49·5	0·754	—	—
Hexamethylene	C_6H_{12}	81·4	0·779	0·506	87
Heptamethylene	C_7H_{14}	118	0·811	—	—
Octomethylene	C_8H_{16}	150·6	0·839	—	—
Nonomethylene	C_9H_{18}	172	0·770	—	—

In addition to the "normal" hydrocarbons of each series there are numerous isomers which come within the boiling range of petrol.

It will be noted that the hydrocarbons of the polymethylene series are of higher gravity than those of the paraffin series of about the same boiling-point, and that the specific gravity in each case increases with rise of boiling-point, whilst the specific heat and latent heat decrease.

The specific gravity alone of a petrol is therefore no true criterion as to its relative volatility, and a distillation test, by which the volume of the fractions obtained between certain fixed temperatures determined, forms at present the most satisfactory basis for a fair comparison. Since the boiling-point is dependent upon the vapour pressure, the higher the proportion of distillates obtained at a low temperature the greater the degree of volatility as a whole.

Crude cracked spirit usually is of yellow colour and the colour deepens on storage; it has a characteristic and unpleasant odour. It differs widely in composition from "straight spirit," chiefly in containing a high percentage of unsaturated hydrocarbons, and generally aromatic hydrocarbons, which are usually only present in straight spirits in small quantities. Cracking of petroleum oils was actually carried out during the war specifically to produce aromatic hydrocarbons, primarily toluene.

In an investigation of a cracked spirit, Brame and Hunter (*J. Inst. Pet. Tech.*, 1927, **13**, 794) found the saturated hydrocarbons to be 67·83 per cent.; unsaturateds, 27·20 per cent.; aromatics, 4·97 per cent. Several members of the paraffin and naphthene series of hydrocarbons were identified and olefines predominated among the unsaturated; di-olefines and cyclic olefines were also recognized.

The reactive unsaturated hydrocarbons polymerize and oxidize in time with the formation of a reddish "gummy" mass, only slightly soluble in the spirit. Refining of cracked spirit is primarily directed to removing these gum-forming bodies. The unsaturated hydrocarbons, other than these of high reactivity, have excellent anti-knock characters (high octane value) and it is therefore desirable to retain these. Chemical treatment of cracked spirit is therefore a matter calling for highly specialized methods, and because of the high re-activity of the unsaturateds must be very carefully controlled. Especially is this the case with any sulphuric acid treatment, and owing to polymerization, etc., occurring and much of the product remaining in solution in the spirit, acid treatment must be followed by re-distillation.

Casing-head spirit is almost entirely composed of the lower boiling hydrocarbons of the paraffin series. Chemical or other treatment is seldom necessary. D. B. Dow (*U.S. Bur. Mines*) gives the following results for the distillation of a raw spirit:

I.B.P.	31° C.	50 per cent. distils	61° C.
10 per cent. distils	32·5°	60 „ „	75°
20 „ „	36·0°	70 „ „	93°
30 „ „	42·5°	80 „ „	143°
40 „ „	50·0°	F.B.P.	143°

The loss on distillation was 18 per cent. This high figure is due to the impossibility of condensing the considerable proportion of very low-boiling hydrocarbons, some of which are originally simply held as vapours in solution.

By the fractional distillation of a natural gas gasoline R. P. Anderson and A. M. Erskine (*Ind. Eng. Chem.*, 1924, **16**, 263) arrived at the following approximate composition:

	Per cent. by volume.		Per cent. by volume.
Propanes and butanes	20	*n*-Hexane	15
Iso-pentane	13	Iso-heptane	8
n Pentane	17	*n*-Heptane	12
Iso-hexane	9	Octane	4

the balance being some 2 per cent. of absorption oil.

Physical Properties of Petrol. Reference has been made already to the density or specific gravity, which may lie between 0·680 and 0·760, and the boiling range. According to Cabot, petrol of 0·698 sp. gr. at 22·8° C. did not show signs of solidification when immersed in liquid air until a temperature of — 122° C. was reached. J. H. Coste (*Analyst*, 197, **42**, 168) gives the solidification temperature of a well-known petrol as — 128° C.

The specific heat of the liquid and its latent heat of vaporization are of importance. The following figures (Table XXXVIII) were obtained for the specific heat between 10° and 30° C. by one of the authors.

TABLE XXXVIII

SPECIFIC HEAT OF PETROL

	Specific gravity.	Specific heat.		Specific gravity.	Specific heat.
American	0·737	0·465	Sumatra	0·722	0·514
„	0·724	0·483	Mexico	0·725	0·493
„	0·712	0·477	Texas	0·744	0·472
Asiatic	0·767	0·450	Roumania	0·740	0·473
„	0·721	0·490	Burma	0·756	0·462
„	0·713	0·512	Borneo	0·772	0·453

Although not strictly proportional to the density, for practical purposes the specific heat may be calculated from $\frac{K}{\text{sp. gr.}}$, K being approximately 0·350.

Lang, Jessel and Steed (*J. Inst. Pet. Tech.*, 1930, **16**, 813) record the physical data for five of the lower-boiling fractions of Miri petroleum, the specific heats of the fractions being expressed as Cals/gm. at 30° C.; 0·4635 (75–100° C. range); 0·4615 (100°–125°); 0·4605 (125°–150°); 0·4582 (150°–175°); 0·4517 (175°–200°). Also Lang and Jessel, *loc. cit.*, 1932, **18**, 850.

The *latent heat of vaporization* of the normal paraffin and polymethylene hydrocarbons, as determined by Maybery and Goldstein (*Amer. Chem. Jour.*, 1902, **28**, 67) has been given on page 210. Græfe (*Petroleum*, 1910, **5**, 569) gives the latent heat of vaporization of crude light oil as 86 calories per gram. Ricardo found the latent heat to be 132–145 B.Th.U. per lb. (equal to approximately 73–80 calories per gram).

According to Holde the *flash-points* for different petrol fractions were:

Distilling between .	50–60° C.	60–78°	70–88°	80–100°	80–115°	100–150°
Flash-point below .	− 58°	− 39°	− 45°	− 22°	− 22°	+ 10°

J. H. Coste (*loc. cit.*) records the following flash-points:

"Standard," − 11° C.; "Shell," − 16° C.; Pratts, − 30° C.

The *ignition temperature* of petrol and petrol-air mixtures has been given on page 7.

Calorific Value of Petrol. Very little difference is found in either the *gross* or *net* calorific value of petrol on a weight basis, the B.Th.U. per lb. for a number of samples examined by B. Blount in 1909 being 20,140 to 20,340 B.Th.U. (*gross*). The *net* calorific values recorded by Ricardo (*J. Soc. Auto. Eng.*, 1922, **10**, 305) are given in Table XXXIX. It is to be noted that spirit of high specific gravity will have a much higher relative calorific value per gallon than lighter spirit of about the same calorific value per lb.

TABLE XXXIX

CALORIFIC VALUE (NET, B.TH.U.) AND LATENT HEAT OF VAPORIZATION OF PETROLS (*H. R. Ricardo*)

Index No.	B.Th.U. including latent heat of vaporization.		B.Th.U. excluding latent heat of vaporization.		Vapour pressure at 0° C. mm. Hg.
	Per lb.	Per gal.	Per lb.	Per gal.	
1	19,020	137,500	18,890	136,600	86
2	19,250	135,500	19,130	134,700	68
3	19,090	137,100	18,970	136,400	70
4	19,120	137,000	19,000	138,100	54
6	18,890	143,500	18,770	142,600	18
7	18,580	145,200	18,450	144,300	28
8	18,920	145,000	18,790	144,100	17

The principal data in reference to petrol are given in Table XL, page 215, together with those of benzole and alcohol, so that a comparison may be instituted between these fuels.

Distillation Characters. When air is bubbled through petrol or passes at ordinary temperatures over a surface saturated with such a liquid of mixed composition, evaporation is selective, the less volatile portions remaining behind, i.e. the petrol becomes " stale." Air passed through petrol at atmospheric temperatures is stated to take up practically only the hydrocarbon hexane (C_6H_{14}). In the early days of the petrol engine carburation was accomplished usually by carburettors of the bubbling or surface-evaporation type, so that a much more restricted range of boiling for the petrol was essential, and its gravity was usually about 0·680. With the introduction of spray carburettors, in which the heavier less volatile portions of the spray get carried forward as a mist into the hot inlet pipe adjacent to the cylinder or to the cylinder itself and there become vaporized, a much greater range is permissible; the gravity of suitable spirit is now frequently 0·760. This improvement is of great economic importance in rendering a far greater proportion of the crude oil available, and further improvements in carburettors will doubtless permit of some extension of the range of boiling in the future.

The desirable characters in a petrol are summarized by Dean (*U.S. Bur. Mines, Tech. Paper* 166, 1917) as:

1. Not too high a percentage of highly volatile constituents, which involve large evaporation losses, increased danger in storage and use. On the other hand, for ease of starting, a reasonable proportion is required.
2. Not too large a proportion of high-boiling hydrocarbons, otherwise condensation in the cylinders occurs, the " heavy ends " are not burned, and dilution of the crank-case oil results.
3. Freedom from water, acid, and anything which on evaporation of the petrol leaves a residue.
4. Freedom from anything which attacks metal before or after combustion.
5. Freedom from objectionable odour.

Many suggestions have been made for assessing the starting characters of petrols on the basis of the distillation tests. Oberfell and Alden (*Oil and Gas J.*, 1933, **31**, No. 35) suggested a " *volatility index* " —the difference between 284° F. and the temperature at which 50 per cent. of the petrol distils. Thus, taking the grades in the specifications (p. 225), U.S. Motor Gasoline = 0; Motor Fuel " V " = 27; Domestic Aviation = 63; Fighting grade = 72.

Bridgeman (*Oil and Gas J.*, 1931, Mar. 5, 143) says that starting should not be difficult until approximately 140° F. below the tempera-

TABLE XL

PROPERTIES OF PETROL, MOTOR BENZOLE, AND ALCOHOL (METHYLATED)

		Petrol.	Motor Benzole.	Alcohol (Methylated).
Specific gravity		0·720–0·740	0·878	0·816
Composition		Paraffin hydrocarbons mainly of C_nH_{2n+2} series Carbon = 84% Hydrogen = 16%	Benzene (C_6H_6) and Toluene (C_7H_8) Carbon = 91·7% Hydrogen = 8·0%	Ethyl alcohol (C_2H_6O) Methyl alcohol (CH_4O) Carbon = 50·7% Hydrogen = 13·0% Oxygen = 36·3%
Boiling range		36–200° C.	70–145° C.	
Freezing-point		About – 120° C.	– 5° C.	About – 110° C.
Coefficient of expansion	per ° C.	0·0008	0·00140	0·00110
	„ ° F.	0·00045	0·00077	0·00062
Specific heat		0·470	0·416[2]	0·615[2]
Latent heat of vaporization (calories)		86·0	94·35 [2]	203·0 [2]
Calorific value	B.Th.U. per lb. (gross)	20,000	8,050	11,815
	„ „ „ (net)	18,450	17,320	10,690
	„ „ gal. (gross)	144,000 [1]	158,480	96,410
	„ „ „ (net)	132,500 [1]	152,000	87,230
Theoretical air for combustion	lb. per lb.	15·24	13·46	8·75
	cu. ft. per lb.	187 (at 0° C.), (197 at 60° F.)	165·5 (175)	108 (113·5)
	b. per gal.	109·6	118·5	71·40
	cu. ft. per gal.	1346 (0° C.), (1420 at 60° F.)	1456 (1540)	886 (930)
Calorific value of 1 cu. ft. of theoretical mixture		103	105	97·5
Explosive range (vapour per cent. by volume in mixture)		1·1–5·3 [3]	2·7–6·3	4·0–13·6
Compression limit in lb.		About 70	Slightly above petrol.	About 200.

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[1] Calculated on assumed gravity of 0·720.

[2] For pure benzene and ethyl alcohol respectively.

[3] Range given in M.U. Fuel Committee Report.

ture (F°) at which 10 per cent. distils, whilst for *easy* starting Brown considers 130° F. below this point is satisfactory.

A satisfactory anti-knock fuel, according to Charpentier (*Aut. Zeit.*, 1933, **126**, 157), should distil at least 30 per cent. to 100° C. and 90 per cent. to between 180° and 185° C.

Too high a percentage of highly volatile components, in addition to certain drawbacks referred to above, will give rise to vapour locks in the fuel supply lines ; especially is this important with air-craft at high altitudes.

Vapour lock is a function of the vapour pressure and the Reid method of measuring this has been adopted as a standard method in the U.S.A. In this apparatus, for fuel to be used up to a maximum temperature of 100° F. the pressure should not exceed 8 lb. ; at 85° F. 10 lb. ; and at maximum 75° F., 12 lb.

In winter-time the petrol should have a higher average volatility than in summer, U.S.A. winter grades usually giving 90 per cent. volatility below 400° F. (204° C.), and summer grades below 450° F. (221° C.), though each of these temperatures is much higher than is found in this country for the 90 per cent. point in good grade spirits.

The last boiling fractions are also of importance, for crank-case dilution of the lubricating oil arises through these portions—only partially burnt—being carried down with lubricating oil past the piston rings. Dilution, although due to these "heavy ends" accumulating in the oil, is far more determined in degree by the condition of the engine (fit of piston rings) and operating conditions (chiefly temperature of the oil in the sump).

Combustion of Petrol. When petrol (assuming the composition C_6H_{14}) is burnt completely with the theoretical amount of air (15·24 lb. per lb.), the dry exhaust gases would consist of carbon dioxide 14·35 per cent., nitrogen 85·65 per cent. It has, however, been noted frequently that after undergoing combustion in an engine it is impossible to account for all the carbon consumed as carbon dioxide and monoxide in the gases, which points to the conclusion that products of incomplete combustion other than carbon monoxide are formed, and aldehydes are produced under some conditions. The formation of carbon monoxide through insufficiency of oxygen is observed frequently when the exhaust gases are analysed, and it has been observed by Clerk that an excess of oxygen may be present even when carbon monoxide is still being formed.

Watson carried out extensive investigations on the petrol engine (see *Engineering*, 1910, **88**, 331 ; *J. Soc. Arts*, 1910, **58**, 988 ; and *Proc. Inst. Automobile Engs.*, 1914–15, **9**, 49), and found that the highest thermal efficiency was not attained when the air for combustion was the theoretical amount, but was obtained actually with an air/petrol ratio of 17 to 1. This is concluded to be due to two causes, a lower cylinder temperature, so that less heat is lost through the walls, and to the lower mean specific heat of the gases (the specific heat rising with the temperature), hence the rise of pressure is greater for a given quantity of heat supplied. In general, the best mechanical efficiency was found with about 12 lb. of air to 1 lb. of petrol. With a weaker mixture than 17·5 to 1 there is risk of back-firing into the carburettor, the rate of burning being so reduced that combustion is not completed before the inlet port opens.

The composition of the exhaust gas from a petrol engine, assuming the fuel to be hexane, C_6H_{14}, requiring 15·24 lb. of air per lb. of fuel, would be: nitrogen, 85·65 per cent.; carbon dioxide, 14·35 per cent. It is found that from most engines the percentage of carbon dioxide is much lower, and that several per cents. of carbon monoxide are present, indicating much waste of fuel. Watson states that 5 to 6 per cent. of carbon monoxide is common. Important investigations of the combustion process have been carried out in the United States by Fieldner, Straub, and Jones (*J. Ind. and Eng. Chem.*, 1921, **13**, 51), and Fieldner and Jones (*loc. cit.*, 1922, **14**, 594). Their results for carbon monoxide in the exhaust gases from engines under actual road test agree with Watson's figures, and in many cases show a waste of fuel, through incomplete combustion, of 20–30 per cent. The use of an over-rich mixture is common; such mixtures enable the engine to be started with fair ease (it is stated that an engine cannot be started cold on the theoretical mixture); further, the richer mixtures give greater power and flexibility. Thermal efficiency, and consequently mileage per gallon, is attained with a considerably higher air/petrol ratio than that required for maximum power. To some extent power must be sacrificed to obtain greater mileage; but in these tests it was found possible to adjust the carburettors to give reasonably good fuel economy without undue sacrifice of power and flexibility. Several cars tested gave good results with air/petrol ratios 13·7/1 to 14·7/1.

A point of importance arising from the production of carbon monoxide is the danger of poisoning by this gas when the engine of a car is run in a small and poorly ventilated garage.

The Petrol/Air Mixture. The theoretical amount of air for the complete combustion of petrol, as deduced from the average composition by methods already described on page 10, is:

		Cubic feet	
	lb.	at 0° C.	at 60° F.
Per pound	15·24	187	197
Per gallon	109·60	1346	1420

One volume of the liquid requires, therefore, 8400 (at 0° C.) to 8900 (at 60° F.) times its own volume of air for complete combustion.

Similarly, the percentage of carbon dioxide in the *dry* exhaust gases for petrol of this composition will be 14·3 per cent.

Owing to the complex nature of petrol, it is not possible to calculate accurately the actual volume in the state of vapour which a given volume of liquid petrol would occupy, as, for example, when it is taken up as vapour in an air current. 1 lb. of hexane would occupy 4·2 cu. ft. in a state of vapour at 0° C. (4·4 at 60° F.), whereas 1 lb. octane would occupy 3·15 cu. ft. at 0° C. (3·32 at 60° F.). Taking a round figure of 4 cu. ft. of vapour per pound of petrol, it will be found that the theoretical air required is about 48 times the volume of the petrol vapour, or the mixture contains practically 2 per cent. petrol vapour.

The calorific value of 1 cu. ft. of the theoretical petrol/air mixture may now be calculated. The total volume of mixture per pound is $4 + 187 = 191$, and the calorific value of petrol per pound is approximately 20,000 B.Th.U., hence $\frac{20,000}{191} = 104{\cdot}5$ B.Th.U. per cu. ft. Similarly, at 60° F. the value per cu. ft. is approximately 99·5 B.Th.U.

Air is able to take up a far greater amount of petrol vapour than the above; dry air will take up 17·5 per cent. by volume of 0·650 petrol at 50° F. (= 1 vol. petrol vapour to 5·7 vols. of air), whilst at 68° F. it will take up 27 per cent. (= 1 vol. vapour to 3·7 vols. of air). It is evident, therefore, that a large excess of air must be employed in practice to bring such a mixture down to theoretical strength.

Further, above a certain percentage of vapour the mixture, although highly inflammable, is not explosive. The range of composition between which mixtures of petrol vapour and air are truly explosive is very limited. The figures given in the " Motor Union Fuels Report " (1907) are : *minimum*, 1·1 per cent. by volume ; *maximum*, 5·3 ; explosive range, 4·2. On the assumption that 1 lb. of petrol gives 4 cu. ft. of vapour, the explosive mixture figures are approximately :

	lb. air.	Cubic feet. at 0° C.	at 60° F.
At maximum for 1 lb. petrol . .	5·76	71·5	74·5
At minimum " " . .	29·0	360·0	375·0

The more generally accepted limits are : *minimum*, 2·0 per cent. ; *maximum*, 4·5 per cent., and these figures are probably more in agreement with the true explosion conditions, as distinct from bare inflammation.

It must be remembered that although a mixture may be non-explosive at ordinary pressure, on increasing the pressure such a mixture may become explosive.

Rate of Flame Propagation in Petrol/Air Mixtures. This is obviously an important consideration, determining as it does whether combustion has ceased before the end of the working stroke of the piston, and how soon after ignition the maximum pressure is reached, which determines incidentally the point in the cycle where ignition should take place. Obviously, with an engine running at, say, 3000 revolutions per minute, a slow-burning mixture may even be alight when the inlet valve opens, with consequent firing back (" popping ") into the carburettor.

The degree of turbulence in the mixture has, however, an important modifying influence in practice, and to a large extent determines a far more rapid spreading of the flame throughout the mixture. Further, turbulence has an important effect in diminishing the liability of a charge to burn with excessive speed, setting up undue pressures and leading to the well-known trouble of detonation or " pinking." The amount of turbulence will depend largely upon engine design, and will be greater with increased piston speeds.

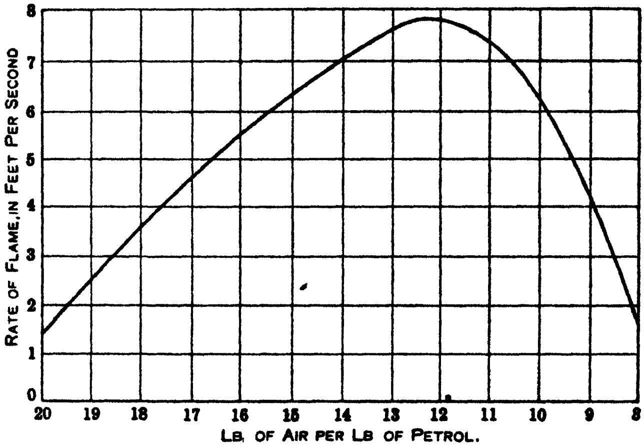

FIG. 43.—Rate of Flame Propagation in Petrol-Air Mixtures (Neuman).

Neuman has made determinations of the rate for petrol/air and his results are shown graphically in Figure 43.

It will be seen that a maximum rate is obtained with about 12·5 parts by weight of air to 1 of petrol, which is considerably less than the theoretical air necessary, and is in fairly close agreement with the mixture giving the best mechanical efficiency.

Chemical Composition and Engine Performance.—The efficiency of an internal combustion engine is directly related to the degree of compression of the gases prior to ignition. For the highest efficiency it is desirable to have the highest practicable compression, but a limit is soon reached. Obviously with a fuel/air mixture over-compression would raise the temperature to that of spontaneous ignition (p. 6) and *pre-ignition* would occur before the timed spark functioned.

In general, before this point is reached trouble is experienced, particularly with rich (and therefore rapid burning) mixtures, through a portion of the charge burning with exceptional rapidity *after* the usual ignition by the spark, giving rise to the well-known " pinking," " knocking," or " detonation." In the early days of the petrol engine it was known that some fuels were more liable to detonation than others and that the addition of benzole overcame or materially reduced the knocking.

H. R. Ricardo (*Eng.*, 1920, **110**, 325, 361 ; *The Automobile Eng.*, 1921, **11**, Feb.–Aug.), using a specially designed engine which enabled the compression of the mixture to be varied during running, made a series of valuable tests on petrols which enabled some correlation to be made between composition and performance. Briefly, Ricardo showed that whilst at moderate compression ratios (5/1) all hydrocarbon fuels give much the same efficiency, because it was possible to work at considerably higher compressions with those containing a high percentage of aromatic hydrocarbons, or naphthenes, considerable gain in efficiency was possible. The limit to higher compressions is directly or indirectly the spontaneous ignition temperature of the charge. For any fuel a practical limit to the degree of compression allowable could be arrived at—the " highest useful compression ratio " (H.U.C.R.). A few of Ricardo's results are given in Table XLI.

TABLE XLI

COMPOSITION OF PETROLS IN RELATION TO COMPRESSION AND CONSUMPTION
(*Ricardo*)

Index No.	Approximate composition.			Highest useful compression ratio.	Temperature at H.U.C.R. ° C.	Consumption at H.U.C.R. per B.H.P. hour.	
	Paraffins	Naphthenes.	Aromatics.			lb.	pints.
7	26	35	39	6·0	430°	0·393	0·402
8	10	85	5	5·9	428°	0·389	0·405
1	62	23	15	5·7	422°	0·393	0·435
6	38	47	15	5·35	410	0·407	0·428
3	68	20	12	4·7	387	0·435	0·484
X.	63	35	1·7	4·85	392	0·422	0·471

X.—A petrol from which aromatic hydrocarbons had been removed.
The Index numbers refer to the fuels quoted in Tables XXXIX and XLII.
It may be noted that Petrols 1 and 3 are of almost identical composition, but exhibit a considerable difference in the highest useful compression ratio.

Ricardo suggested that this " anti-knock " quality might be expressed in terms of the equivalent " toluene value " of the fuel, this hydrocarbon having the greatest influence of the three—benzene, toluene and xylene. By a fairly simple analytical method an approximation of the amount of each aromatic hydrocarbon in the petrol can be determined and from the data the "toluene value" calculated.

Octane Numbers. Following on Ricardo's work, which first showed the importance of the nature of the hydrocarbons in petrol in determining the combustion characteristics, there were developments in the direction of measuring the "anti-knock" value, using variable compression engines. This work has now been satisfactorily standardized and agreement reached between the principal standardizing bodies in the United States and in this country. Not only must the engine and procedure be standard, but a standard of reference for the different fuel agreed upon. This is the "octane number."

Pure *iso*-octane (2 : 2 : 4—trimethylpentane) (C_8H_{18}) was first suggested as a standard of very high anti-knock character by Edgar (1931); the converse, a hydrocarbon of high knocking character, being *n* heptane (C_7H_{16}). Their respective boiling-points are approximately the same (99° C.).

Assessing the anti-knock value of *iso*-octane as 100, and that of *n* heptane as 0, the "octane number" is numerically the percentage by volume of iso-octane in an octane/heptane mixture which matches the petrol by its detonation characteristics in the engine test. Thus with a 70/30 octane/heptane mixture matching the fuel the "octane number" of that fuel is 70.

On this scale the "octane numbers" of motor fuel are approximately:

Alcohol racing mixture . .	85 +	No. 1 Petrol	68–70
Petrol with lead tetraethyl .	77	Commercial Petrol . . .	60–66

According to Boyd (*Amer. Pet. Inst.*, 1931), in the standard test engine at full load, 600 r.p.m. and a jacket temperature of 212° F., with the mixture ratio and spark advance set for maximum power, the following data show the permissible compression ratio for the corresponding octane numbers:

Octane number.	Compression ratio.	Octane number.	Compression ratio.
98·5	7·0	67·5	4·0
92·5	6·0	50·0	3·5
84·2	5·0	40·0	3·4
78·0	4·5		

It is claimed that close correlation between road results and the standard engine are obtained with the latter at 900 r.p.m. and with a jacket temperature of 300° F.

For the British Air Ministry specification D.T.[illegible] 134, for some years the standard, the octane number was 73; more recently (D.T.D. 224) it was raised to 77, and the still higher value of 87 is to be specified in D.T.D. 230.

For civil aviation the octane numbers range from 70 to 73.

Anti-knock Agents. Certain organic compounds have been found to have the property of suppressing knocking; conversely, certain others induce it. Midgley and Boyd (*Ind. and Eng. Chem.*, 1922, **14**, 589; 894) found that aromatic amines, in general, belong to the former class, but that the most effective agents were organo-metallic compounds. Thus, compared with benzene, xylidine was 12·5 times as effective; di-ethyl telluride [$(C_2H_5)_2$ Te], 250 times; lead tetraethyl [$(C_2H_5)_4$.Pb], 625 times. Carbonyls (e.g. iron) are also materials for which patents have been taken out.

Lead tetraethyl is most widely used, the quantity required being very small, a concentration of 1 in 1000 to 1400 giving sufficient anti-knock effect for general use, though for air-craft engines higher concentrations are employed.

Lead tetraethyl has the great disadvantage of being highly poisonous, and as the result of several casualties in the early days it was for a time withdrawn, but after an exhaustive inquiry in the U.S.A., with resulting control of production and distribution, its use became general, and, providing reasonable precautions are observed, such as avoiding undue contact with the skin, little risk is involved. The "ethyl" petrols are usually given a distinctive colour.

Another point is that the lead oxide resulting from the combustion affects the sparking plugs, and to overcome deposition of the metal some chlorine or bromine compound is added, thus a mixture of 3 volumes of lead tetraethyl and 2 volumes of ethylene di-bromide has been widely used. Carbon tetrachloride and trichloroethylene have also been used.

A valuable paper on lead tetraethyl in fuels for aviation engines was contributed to the Royal Aeronautical Society by F. R. Banks (*Pet. Times*, 1934, **31**, 97), in which it was stated that the addition of the first cubic centimetre to a gallon of petrol will raise the anti-knock value by anything from 5 to 15 octane numbers, depending on the characters of the petrol. Further, that the maximum concentration of tetraethyl, for commercial purposes, is 3·6 c.c. per Imperial gallon, which may be raised to 7 c.c. for Government or military purposes.

Ethyl fluid, in which form the mixture is prepared, contains:

Lead tetraethyl	61·42	per cent.	(by wt.)
	= 65·50	,,	(by vol.)
Ethylene dibromide	35·68	,,	(by wt.)
Dye (blue)	0·17	,,	

The specific gravity of the ethyl fluid is 1·755 (20° C.).

The use of lead tetraethyl has given trouble through corrosion of exhaust valve stems, cylinder walls, and also in exhaust pipes and collector rings. According to Mardles, the combustion product is lead oxybromide ($PbBr_2PbO$), which hydrolyses with moisture to form corrosive substances. After running, injection of oil into the cylinder and a weekly turning of the engine counteracts corrosion. The U.S. Air Force uses castor oil with the addition of 2 or 3 per cent. of triethanolamine.

Gum in Petrol. As already mentioned, "cracked" spirits are liable to go off colour, becoming yellow, and in untreated spirit this may occur to such a degree that a brown resinous deposit forms in any vessel. This is the "gum," which is only slightly soluble in petrol, yet even this low solubility will give rise to a deep straw colour. It is generally easily soluble in alcohol.

Gum in petrol may lead to sticking up in carburettors and of inlet valves and the formation of deposits in inlet manifolds. In specifications the inclusion of some limit to the gum is usual, and is important to-day with the wide use of blends containing cracked spirit. In the Western Petroleum Refiners' Association specification this limit is 30 mgm. per 100 ml. The British Air Ministry will be found on page 224, and the United States Federal specifications limit on page 225.

Gum is referred to as "pre-formed" and "potential." The former, or existent gum, is that present when a sample of spirit is analysed by evaporation ; potential gum is the additional gum which can be formed by oxidation treatment. It is roughly a measure of the residual so-far unchanged active unsaturated bodies. Except in some exceptional cases gum is a complex mixture of the oxidation products of highly reactive unsaturated hydrocarbons. Polymerization also plays a part in gum formation, and is favoured by light.

Comie considers that the "gum forming materials" (*pseudo-gum*) consist largely of peroxides, per-acids, aldehydes and ketones, and gum formation to be a process of auto-oxidation, the resinous substance remaining after evaporation being of ester or lactone structure.

Gum formation may be inhibited by a number of organic compounds, bodies themselves readily oxidized. Amongst these are alpha-naphthol, catechol, ortho-aminophenol, mono- and di-benzylparaaminophenol, the latter said to be effective in concentration not exceeding 0·005 per cent.

The effect of contact with alkalies is in some cases of importance, as this affects the colour-maintaining properties of the petrol. Where petrol treated with inhibitors is stored over water it is recommended to add 0·1 per cent. of sodium sulphite to the water.

The liability to the formation of gum has been investigated by Voorhees and Eisinger by an oxygen absorption test, in which the sample is heated in stout glass bottles with oxygen at 210° F. for five hours. An " induction " period is found with petrols, after which the formation of gum proceeds more and more rapidly. Mardles considers results under the above conditions of temperature and oxygen concentration are not satisfactory and employs a method in which 50 ml. of the sample are heated to only 35° C. in a 500-ml. flask, filled with air, for twenty hours, the gum formed being then determined. Results are stated to be in accord with the results on storage for three months.

Motor Spirit Specifications. Standard methods for the analysis of petrols (and other petroleum products) have been published by the Institution of Petroleum Technologists. The principal test for motor spirit is a distillation test under carefully standardized conditions. Besides the percentage of distillate collected at certain temperatures, the Initial Boiling Point (I.B.P.) and the Final Boiling Point (F.B.P.), i.e. when the flask is dry, are very important. The standard method is described on page 358. In addition, the presence of acidity (indicating faulty refining), the liability to cause corrosion, the absence of any non-volatile residue, and the presence of certain types of sulphur compounds, are also important. The British tests also include the determination of the percentage of aromatic hydrocarbons, and " gum," the importance of which since the introduction of " cracked " spirits has become important.

The following is a summary of the petrol specifications in Great Britain and for the United States of America Government:

Earlier Air Force Specifications were:

Aviation Spirit 0·720 (not to exceed 0·740).—10 per cent. below 75° C; 60 per cent. below 100°; 95 per cent. below 140°. Aromatic content, 12–20 per cent. by volume.

Aviation Spirit 0·760 (not to exceed 0·790).—10 per cent. below 75° C; 50 per cent. below 100°; 90 per cent. below 150°. Aromatic content, not less than 35 per cent.

The Air Ministry Specifications D.T.D. 224 for 77 octane and D.T.D. 230 for 87 octane Standard Fuels for Aero-Engines are practically identical except as regards anti-detonation value. In both cases the standard fuel shall consist of high-grade petrol prepared from crude petroleum, coal spirit or mixtures thereof, and that the fuel as a whole shall be neutral, clear, free from undissolved water and suspended matter.

In D.T.D. 224, in order to obtain the necessary anti-detonation, aromatic hydrocarbons may be added, the extent of such additions being governed by the succeeding clauses of the specification. In D.T.D. 230 it is permissible to add aromatic hydrocarbons and/or tetraethyl lead not exceeding 4 ml. per imperial gallon.

In each case the distillation range is specified as follows: When

100 ml. of the fuel are distilled in the standard distillation apparatus, there shall distil at 760 mm. pressure:

Below 75° C. not less than 10 per cent.
At 100° C. not less than 50 per cent.
At 150° C. not less than 90 per cent.
The end point shall not exceed 180° C.
The distillation loss shall not exceed 2 per cent.

The total volume of distillate collected in the receiver shall not be less than 96 per cent.

Both specifications state that: The vapour pressure as determined by the Reid method of 37·8° C. (100° F.) shall not exceed 7 lb. per sq. in.; the specific gravity at 15° C. shall not be more than 0·79; and there shall be a complete absence of free sulphur when determined by the copper strip method and the total sulphur content shall not exceed 0.15 per cent. by weight.

The freezing point as indicated by the initial formation of solid shall not be higher than minus 50° C. in the case of 77 octane standard fuel, and minus 60° C. for the 87 octane fuel.

The gum standard is indicated in both cases. The existent gum shall not exceed 10 mgm. per 100 ml. Potential gum.—After 50 ml. of the fuel have been incubated at 35° C. for twenty hours, the increase of gum yield over and above the existent gum shall not exceed 10 mgm. per 100 ml.

The U.S.A. Federal specifications are as follows:

Distillation.	Aviation.		U.S. Motor.	Motor V.
	Domestic.	Fighting.		
10 per cent. not above . .	75° C.	75° C.	75° C.	70° C.
50 ,, ,, . .	105	100	140	125
90 ,, ,, . .	155	135	200	180
96 ,, ,, . .	175	—	—	—
End Point	190	—	—	—
Freezing-point	– 60	– 60	—	—
Sulphur, per cent	0·10	0·10	0·10	0·10
Gum	15 mgm. (2 hrs. glass)	10 mgm. (4 hrs. glass)	—	—
Vapour pressure at 100° F. (lb. per sq. inch)	6·5	6·5	8–12	10
Octane number	58	87	—	—

The distillation range of a number of petrols, ranging from light aviation spirit to heavy commercial motor spirit, is given in Table XLII. The samples were among those employed by Ricardo in his researches (p. 220).

TABLE XLII

Distillation Range of Petrols (Engler Method)

(*H. R. Ricardo. The Automobile Eng.*, 1921)

Index No.	Specific Gravity.	Percentage distilling below						Final Boiling-point °C.
		80°	100°	120°	140°	160°	180°	
1	0·723	41·3	79·0	99·0	—	—	—	126
2	0·704	28·0	65·0	86·5	94·5	—	—	153
3	0·719	16·5	43·0	71·0	86·0	96·0	—	170
4	0·727	11·5	47·0	79·0	92·0	98·5	—	160
5	0·750	7·0	24·0	47·0	67·0	81·5	91·0	210
6	0·760	—	13·0	66·0	89·0	97·5	—	166
7	0·782	—	15·0	54·0	83·0	96·0	—	164
8	0·767	—	7·0	55·0	83·0	94·0	—	176

From a series of distillation tests on petrols of well-known brands marketed in 1933 the following data has been compiled : Initial boiling point, 34–40° C. ; 10 per cent. distilled below 59–68° C. ; 20 per cent. below 74–80° ; 50 per cent. below 106–115° ; 90 per cent. below 153[1]–172° ; end boiling-point 172[1]–199°. The percentage distilled at 100° C. ranged from 38–44.

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[1] These figures are exceptionally low and are for one particular brand.

CHAPTER XI

MOTOR BENZOLE, ALCOHOLS AND FUEL MIXTURES

"MOTOR BENZOLE"

Large quantities of "motor benzole" are produced from the distillation of coal, chiefly in the gasworks and coke-oven plants of the country. There is naturally some fluctuation in the yearly production but it may be taken as exceeding 30 million gallons in Great Britain. As indicative of the importance of benzole for motor purposes approximately 90 per cent. of the total production is marketed as motor fuel. The world production of benzole is a little short of one million tons.

In 1919 the National Benzole Association was formed, and has done much to advance the use of this home-produced fuel, carrying out valuable research work on production, refining, and other problems associated with its use. Under the auspices of the Association a valuable treatise has been published.[1]

The hydrocarbons in benzole are chiefly of the benzene series—benzene (boiling-point 79·6° C.), toluene (110·5° C.), xylenes (137·7–144° C.). In addition there are paraffin, naphthene and unsaturated hydrocarbons, including certain di-olefines, the latter very undesirable constituents being responsible for the raw material going off colour and the formation of "gum." Unsaturated olefinic hydrocarbons are not objectionable, indeed they have a definite anti-knock value, as in gasolines.

Commercial benzole is classified as 90 per cent., 50 per cent., 50/90 per cent., etc. This does not indicate the percentage of benzene present in the distillate, but the percentage distilling below a certain temperature, generally 100° C. Thus, a 90 per cent. distillate yields 90 volumes out of 100 up to a temperature of 100° C.; 50/90 yields 50 volumes up to 100° C., and 90 volumes, in all, before 120° C. is exceeded.

It follows that the commercial grades are mixtures of the hydrocarbons benzene, toluene, and xylene, the proportion of the last two increasing as the yield below 100° C. decreases.

For the commercial benzole obtained from high-temperature tars the following proportion of the hydrocarbons present may be taken as approximately correct:

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[1] *Motor Benzole*, by W. H. Hoffert and G. Claxton.

	Benzene.	Toluene.	Xylene.	Other hydrocarbons.
90 per cent. benzole .	70–75	22–24	traces	4–6 per cent.
50 per cent. benzole .	50	35–40	10	

Refined motor benzole consists approximately of benzene, 70 per cent.; toluene, 18 per cent.; xylenes, 8 per cent.; aliphatic hydrocarbons, 3·5 per cent.

Formerly practically the whole of the benzole and toluole (from which the pure benzenes and toluenes were obtained) was produced by the distillation of the tar. To-day by far the greater production is from the coal gas, the hydrocarbons either being scrubbed out by a suitable high-boiling solvent (hydrocarbon wash oils or a creosote oil) or by adsorption by active carbon.

Naturally the quantity of benzole, toluole, etc., obtainable from tar is variable; the type of coal and conditions of carbonization (temperature, type of retort, etc.) affect this. An average figure may be taken as 10–10·5 gals. of motor fuel and 5·75 gals. of solvent naphtha per 1000 gals. of dry tar, equal to approximately 0·1 gal. per ton of coal.

From the gas much larger yields are obtained, an average figure of 3 gals. per ton of coal being a fair one for coke-oven practice, where the recovery from the gases has been more widely practised. Yields as high as 4·5 gals. are now being obtained by careful control of cracking conditions.

Distillation of Tar. The crude tar on distillation yields as a first fraction the light oils and naphthas. These are redistilled, and the lowest boiling fractions collected separately. These are washed by agitating thoroughly with sulphuric acid (which removes some sulphur compounds, basic compounds, and certain unsaturated hydrocarbons) then with sodium hydroxide (caustic soda), which removes any tar acids, such as carbolic acid, which may be present, and finally with water. It is then submitted to a process of rectification in stills fitted with apparatus so that whilst the lower-boiling and more volatile constituents pass forward to the water-cooled condensers, the higher-boiling portions are flowing back continually to the still. According to the character of the commercial fraction desired, so the distillates are collected up to a certain temperature and specific gravity.

Recovery from Coal Gas. The oil-scrubbing process consists briefly in subjecting the gas stream to washing with a solvent which has such a high initial boiling-point that the dissolved benzole vapours may be conveniently separated by distillation from the solvent oil. The plant is of simple design, involving gas scrubbers from which the absorbing oil carries the benzole, etc., to steam-heated stills. After de-benzolizing the wash-oil it passes through coolers and thence back to the scrubbers.

During the war it was made compulsory to treat coal gas by scrubbing to recover toluene, principally, and benzene, both being in great demand for the production of explosives.

Adsorption by active charcoal is even simpler in principle, the gas being passed through the granular absorbent, placed in containers provided with coils, through which cooling water circulates during adsorption, and steam to heat up prior to driving out the adsorbed hydrocarbons by the direct passage of live steam.

The largest benzole recovery plant has been installed at the Becton works of the Gas Light and Coke Co. It is an active-carbon plant and can treat 75 million cu. ft. of gas per twenty-four hours, to give 16,000 gals. of benzole. When fresh the carbon can absorb up to 30 per cent. of its weight of hydrocarbons, but polymerization of unsaturated compounds reduces its activity and when this reaches an uneconomic point the absorbent is removed from the system and regenerated by steaming at a red heat in a suitable retort. Eight cylindrical absorbers are provided, and when working at full capacity five are absorbing in parallel, two are being steamed, twenty to thirty minutes being required, whilst the remaining one is either re-charging or standing by.

It is estimated that 2·5 gals. of hydrocarbons can be extracted per 10,000 cu. ft. of gas; equal to approximately 3·25 gals. per ton of dry coal carbonized.

At Devonport, oil scrubbing yields 3·09 gals. per ton of coal; from this crude product 2·89 gals. of rectified benzole is obtained. The rectified benzole has a specific gravity of 0·8825. The first "drip" point on distillation is 78° C.; 86 per cent. distils at 100° C.; 94·5 per cent. at 120° C.

Rectification. The crude benzole obtained from the gas is usually water-white in colour and contains approximately: benzene, 50–55; toluene, 13·5–15·5; solvent naphtha, 3·5–5·5; creosote, 15·0–17·5; unsaturated hydrocarbons, 7–9 per cent.

The crude product is re-distilled, the fore-runnings being rejected and the distillate collected between 70° and 150° C.

As already mentioned, the presence of unstable unsaturated hydrocarbons causes the spirit to colour and gummy substances to be formed, as is the case with the "cracked spirits" from petroleum (p. 211), leading to similar engine troubles if the gum-forming components are not removed or inhibited.

The usual treatment is washing with strong sulphuric acid, followed by alkali and water washes, which treatment removes practically all the unsaturated hydrocarbons. The washing losses may be from 10 to 15 per cent. A further distillation follows. As the bulk of the unsaturated hydrocarbons are non-gum forming and have a distinct anti-knock influence on the fuel, their removal is undesirable. Alternative treatments have been tried—adsorption of the reactive bodies by silica gel and the action of ferric sulphate with an adsorbent clay (Instill).

It has been found that certain compounds act as "inhibitors," even when added in quite minute quantities, and these are now widely used, thereby reducing the refining necessary. One of the most successful of these is "tricresol" (a mixture of the three isomeric cresylic acids), the best concentration being about 0·03 per cent.

According to Hollings and Hay (*Chem. and Ind.*, 1934, **53**, 155) benzole obtained by carbon absorption contains from 0·7 to 1·35 per cent. of sulphur (as CS_2) and sulphur in other forms 0·44 to 0·55 per cent.; that by oil scrubbing 0·25 to 0·4 per cent. (as CS_2) and 0·3 to 0·5 per cent. in other forms.

Use as Fuel. Motor benzole is seldom used alone as fuel, it is generally employed in admixture with gasoline (petrol) as "benzole mixture." Alone benzole has three disadvantages, a freezing-point which is too high; the "first drop" temperature is not far below 80° C., whilst that of gasolines is about 40° C.; and it is somewhat difficult to burn without soot.

Ease of starting an engine depends largely upon the proportion of low-boiling components, roughly indicated by the temperature at which the first drop falls from the condenser during a distillation test. As mentioned above, in this respect benzole is at a disadvantage with petrol.

On the other hand, at the upper end of the distillation range whilst most petrols have an "end point" about 200° C., motor benzoles usually are completely distilled at about 145°–150° C.

This upper limit cannot well be exceeded since it is very difficult to refine the hydrocarbons boiling at a higher temperature sufficiently to prevent the development of yellow colour and resinification on storage. Further, the exhaust gases have an objectionable smell.

An incidental advantage of benzole containing little boiling above 150° C. is that crank-case dilution of the lubricating oil in an engine is less liable than with gasoline.

The National Benzole Association's specification for motor benzole is given below:

	N.B.A.
Specific gravity (60°/60° F.)	0·8700.–0·8850
Distillation not less than	60 ml. at 100° C.
	85 „ „ 120° C.
	95 „ „ 145° C.

The residue on remaining at 0° C. for thirty minutes shall not solidify.

The crystallizing point should not be above — 5° C., and the sulphur content not more than 0·4 per cent., with no free sulphur. A useful test for the latter is shaking with a little mercury, when the latter is coloured brown by sulphides, although the test is interfered with somewhat by other impurities.

Petrol engines have been run with some success with 90 per cent. benzole as the sole fuel. In an exhaustive trial made with a 12-H.P. stationary engine, benzole proved 12·5 per cent. more efficient than petrol. Brewer states that a 40 H.P. 6-cylinder Napier car gave a ratio of miles per gallon on benzole as compared with petrol of 1·25 : 1. In a record of trials given in the M. U. Fuels Reports the ratio for similar trials was 1·36 : 1.

Benzole is used as a fuel almost entirely in admixture with petrol; sometimes with alcohol. Petrol/benzole mixtures have the advantage of higher "anti-knock" properties than straight petrol alone.

ALCOHOL

The necessity for careful consideration of ethyl alcohol as a fuel is crystallized in a simple statement that it is at present the only medium through which man is able to convert the heat energy of the sun into work in a sufficiently reasonable time and in sufficient quantities to justify the application of the term "fuel" to the product. For all other fuels mankind is dependent, sooner or later, on natural materials, the provision of which by Nature is not proceeding at anything approaching the rate of consumption; indeed, in some cases the provision has probably ceased already. Alcohol, either methyl or ethyl, then, is the only fuel which can be manufactured in large quantities without recourse to existing fuel substances, and this possibility is of the utmost importance in countries devoid of any large quantity of natural oils suitable for internal combustion engines. It affords the only possible weapon of defence against increasing cost of imported fuel, and the almost certain increase in the cost of benzole when its use becomes more general. At some distantly future date, when our coal-measures are nearing exhaustion, it may become the fuel on which the nation will be primarily dependent.

Although the quantity of alcohol used in this country as fuel for internal combustion engines is but a very small percentage of the whole, its use has been extending considerably in recent years. Its practical value has been demonstrated abundantly, for it has taken a place already as a commercial fuel in Germany, France and, to a less extent, in the United States. In each of these countries Government aid has been given in investigating methods of production and application in suitable engines. In some countries the use of a proportion of alcohol has been made obligatory, in others the support of State-produced alcohol has been achieved by making compulsory the purchase of a quantity of home-produced alcohol which is a percentage of the total motor spirit used in that country. Thus in 1930, in Germany, alcohol had to be purchased by the petroleum fuel importers up to 2·5 per cent. of the importation, and this was subsequently raised to 6 per cent. Although the United States probably is provided more abundantly by Nature with fuels than any other country, its Government has not hesitated to expend considerable sums in investigating the value of alcohol, and the Report on the subject (Bull. No. 392, U.S. Geol. Survey, 1909) is worthy of careful study. No less than 2000 tests on gasoline and alcohol engines were carried out.

Advantages and Disadvantages of Alcohol. Alcohol as a fuel offers the advantages of great safety, by reason of its low degree of volatility and higher flash-point, about 17° C. (65° F.); its vapours are not quite half as heavy as those of petrol, so that it does not creep and accumulate in dangerous quantities on low levels, and a higher proportion is needed to form an explosive mixture; it mixes in all proportions with water, and burning alcohol can be extinguished with water. Although of much lower thermal value than petrol and benzole, it shows a relatively good thermal efficiency, and the actual consumption for a given power is not much higher than with these other fuels. Its uniformity of composition is another point in its favour.

The higher degree of safety renders the storage, handling and transport of alcohol more free from those necessary restrictions which have to be imposed on petrol and benzole, and would appreciably affect insurance rates. Further, in many hot countries the use of the more volatile spirits is almost impossible, whilst in the hottest climate alcohol is perfectly safe.

On the other hand, there is the great problem of cost and exemption from many of the restrictions at present imposed on its production to be overcome. Further, as minor objections, come the question of possible corrosion; the fact that some 5·5 per cent. of the total heat of its combustion is required for vaporization, and that some addition, such as benzole, or the prior running of the engine on either petrol or benzole to warm up is necessary before alcohol can be used directly. The corrosion trouble is not serious, neither is that of vaporization, once the engine is hot, for there is always the sensible heat of the exhaust gases available; but that of difficulty in starting from the cold is almost inherent in a fuel of low vapour pressure.

Alcohol is too costly in comparison with other internal combustion engine fuels to be used alone; it is blended usually with petrol or benzole. These mixtures are referred to later (p. 242), but a point of importance is that for their preparation nearly anhydrous alcohol is necessary, otherwise separation of components takes place. Thus at 60° F. separation occurs with alcohol/petrol—10 per cent. alcohol, when 0·1 per cent. of water is present; 20 per cent. alcohol with 0·33 per cent. water; 30 per cent. alcohol with 0·57 per cent. water; 40 per cent. alcohol with 1·0 per cent. water. Lower temperatures favour the separation. The strongest alcohol which can be produced by simple distillation contains 95·6 per cent. by weight, or 97·2 per cent. by volume.

Removal of the remaining water to produce practically anhydrous alcohol is now economically possible, one method being by distillation with benzene. The commercial production of water-free alcohol has definitely advanced the position of alcohol as a fuel and alcohol mixtures are readily available.

Composition of Alcohols. A large number of bodies having certain characteristics, which are typified in the ordinary ethyl alcohol of fermentation, are classed as alcohols, but only the first two members of the series, which may be regarded as hydroxyl (OH) substitution products of the paraffin hydrocarbons methane (CH_4) and ethane (C_2H_6), demand consideration as fuel. One very important point is that in all alcohols there is a fairly high proportion of oxygen which affects their calorific value adversely. The composition and physical properties of the fuel alcohols are as follows:

Name.	Formula.	Percentage composition.			Specific gravity.	Boiling-point.
		Carbon.	Hydrogen.	Oxygen.		
Methyl alcohol	$CH_3{\cdot}OH$	37·5	12·5	50·0	0·8102	64·7° C.
Ethyl alcohol	$C_2H_5{\cdot}OH$	52·2	13·0	34·8	0·7946	77·8° C.

The *specific heat* of ethyl alcohol is 0·615 at 30° C. Its *latent heat* of vaporization is 204·5 cals. per gram. The latent heat of methyl alcohol is 263 cals. per gram. Both mix perfectly with each other and with water in any proportion, a marked contraction in volume taking place in the latter case.

Methyl Alcohol (Methanol). For special racing fuels this alcohol is frequently employed, and an air-speed record was set up with a blended fuel the major constituent of which was methanol. Formerly it was obtained entirely by the distillation of the pyroligneous liquids obtained in the destructive distillation of wood (see p. 28). These acid liquids are washed first with alkalies, and the remaining crude spirit contains about 80 per cent. of methyl alcohol or "wood spirit."

Large quantities of methyl alcohol, of exceptional purity, are now made by synthesis, the direct combination of carbon monoxide and hydrogen under pressure in the presence of a catalyst such as zinc oxide. The two gases are cheaply obtainable from "water gas" (p. 288).

$$CO + 2H_2 \longrightarrow CH_3{\cdot}OH.$$

In 1934 the production by synthesis in the U.S.A. was over 12·5 million gallons, nearly four times the quantity produced by the wood distillation process.

The use of methanol as a motor fuel has been the subject of a valuable paper by Howes (*J. Inst. Pet. Techs.*, 1933, **19**, 301). Its low calorific value (9605 B.Th.U. *gross*, 8515 B.Th.U. *net*) determines a high fuel consumption, a factor against its use for long-distance travel, but its higher thermal efficiency, with the much greater volumetric efficiency, due to its high latent heat of vaporization (263 cals./gm. at boiling-point), give to it exceptional advantages. In unsupercharged engines it has been used at the exceptionally high compression ratio of 15/1.

Its miscibility with hydrocarbon fuels is somewhat limited; with aromatic hydrocarbons (particularly benzene) it is much more miscible than with paraffins. Its value as an anti-knock fuel when added to petrol is nearly twice that of benzene. A typical blend is petrol, 70; benzole, 20; methanol, 10 parts.

Ethyl Alcohol (Ethanol) is the principal alcohol obtained in ordinary processes of alcoholic fermentation; small amounts of alcohols of higher molecular weight—the fusel oils—are produced simultaneously. With the realization of the possibilities of alcohol as a fuel much attention is being paid to cheap methods of production; these are referred to in detail later.

Because of necessary Excise restrictions, alcohol for commercial use must be rendered undrinkable by the addition of various other liquids, a process termed *denaturing*. The strength of alcohol is estimated in this country, France and the United States in percentages by volume; in Germany, in percentage by weight. Proof spirit derives its name from the old test of whether the alcohol-water mixture burnt with sufficient intensity to ignite gunpowder. Proof spirit contains 57·06 per cent. by volume, or 49·24 per cent. by weight of alcohol. Its specific gravity at 15° C. is 0·9198. Absolute alcohol is equivalent to 175·35 per cent. of "proof spirit."

Production of Alcohol. The employment of alcohol as a fuel for internal combustion engines must be dependent almost entirely on its cost of production in relation to competitive fuels (petrol and benzole), and this relationship may be of considerable diversity in different parts of the world. Climatic conditions will be an important factor in the prolific production of fermentable material; on the other hand, with rival fuels of mineral origin, costs may be so high locally that alcohol may be the cheaper fuel. These considerations are of great importance in connection with the development of commercial aviation.

The production of alcohol may be from three sources, (*a*) sugars, or starches capable of conversion to fermentable sugars, derived from plants, (*b*) cellulosic material which also may be converted into fermentable bodies, (*c*) " synthetic " alcohol, i.e. alcohol obtained by chemical actions independent of fermentation (e.g. from the ethylene extracted from coke-oven gas, and from acetylene).

Several of the monhydric alcohols are now produced by synthetic methods. Reference has been made (p. 234) to the manufacture of methyl alcohol from carbon monoxide and hydrogen. Among the methods for the production of ethyl alcohol by such processes the principal one is from ethylene; one large corporation in the United States of America made 7 million (wine) gallons from this source in 1932. The ethylene may be obtained from coal or coke-oven gas and a rich source is the gas from petroleum cracking plants (p. 208).

For detail of methods of production and estimated costs of power alcohol the reader is referred to G. W. Monier Williams' *Power Alcohol*; the Inter-Departmental Report on Power Alcohol, *Cmd.* 218 (1919); Fuel Research Board Inter-Departmental Report, " Fuel for Motor Transport," 1920; W. R. Ormandy (*J. Inst. Pet. Tech.*, 1918; *J.S.C.I.*, 1920, 302, R.); " Alcohol for Power Purposes," Sir F. L. Nathan (World Power Conference—*Fuel*—1928).

The economic aspect of alcohol production cannot be discussed at any length. Briefly, fermentation processes demand raw material, which, except in the case of molasses, has a foodstuff market value in this country too high for such material to be extensively used. Considerable quantities of alcohol are produced in large wood-producing countries (Canada, U.S.A., Norway, Sweden) from waste wood and sulphite liquors from the wood pulp factories. In Germany there has been extensive production from potatoes. There is also a moderate production of synthetic alcohol in Switzerland and Norway, where carbides can be produced cheaply by water power, and considerable extension of the plants is being made.

Denatured Alcohol. Various denaturing fluids are employed in different countries for rendering alcohol unpalatable. In England 10 per cent. of crude wood naphtha, largely methyl alcohol, and 0·375 per cent. of mineral naphtha, are employed, the denatured spirit being coloured by the addition of methyl violet. The naphtha causes turbidity when the methylated spirit is diluted with water. For certain purposes, where the presence of mineral naphtha is objectionable, it is omitted, and the wood naphtha reduced to 5 per cent. This " industrial " or non-mineralized spirit is not coloured, but its sale is subject to certain restrictions.

Excise restrictions as to production, denaturing, storage, and sale of alcohol for power purposes were for a long time a serious obstacle in this country to investigations on any scale of the possibilities of alcohol as a fuel, and these restrictions were practically prohibitive to the practical use of alcohol. A most important step was taken under the Finance Act of 1921 whereby much more freedom was given and a special "power spirit" was permitted. Power alcohol must consist of alcohol not less than 66 per cent. over proof (approximately 95 per cent. alcohol by volume); wood naphtha, 2·5 per cent.; crude pyridine, 0·5 per cent.; benzole, 5 per cent. The power alcohol must be coloured red by the addition of 0·75 oz. of eosin (yellow shade) and 0·25 oz. of "Spirit Red 3" to every 1000 gallons.

Before issue from bond at least 25 per cent. of benzole, petrol, or other approved substance must be mixed with the "power alcohol," unless it contains not less than 25 per cent. of denatured ether added in the course of manufacture.

"Power alcohol" can be imported in bulk under Customs supervision at certain specified ports and stored in approved tank warehouses. When the above additions have been made (also under Excise supervision) the spirit may be distributed without further restriction.

In France the denatured alcohol is very similar in composition, but for power alcohol a new denaturant was introduced in 1933 in which 0·6 grams of anthracene dissolved in 1 litre of benzole with 0·2 grams of ethylboric ether is added to the hectolitre of alcohol. In Germany two classes of denatured spirit are available; for ordinary use, 2·5 vols. of methyl alcohol in 100 of ethyl, together with a small quantity of the pyridine bases extracted from coal tar; for fuel purposes, half this quantity of methyl alcohol and not less than 2 per cent. of benzole, the mixture being given a distinctive colour by the addition of methyl violet—one of the coal-tar colours.

Calorific Value. The values determined by different observers differ somewhat—possibly due chiefly to small variations in the strength of the alcohols and admixtures, but the figures below are selected as being most reliable.

Alcohol or mixture.	Specific gravity 15° C./15°.	B.Th.U. per lb.		B.Th.U. per gallon.	
		Gross.	Net.	Gross.	Net.
Methyl alcohol . . .	0·796	9,605	8,515	76,456	67,780
Ethyl alcohol . . .	0·794	12,820	11,690	101,800	92,820
Methylated spirit . .	0·816	11,815	10,690	96,410	87,230
Alcohol 77% Benzole 22·5% . . .	0·832	14,010	12,900	116,560	107,330

According to Schöttler, ethyl alcohol of various strengths has the following density and calorific value :

Alcohol per cent. by vol.	Specific gravity.	Net heating value.
95	0·805	10,880
90	0·815	10,080
85	0·826	9,360
80	0·836	8,630

Shave (*Eng.*, 1920, **110**, 623) gives the following values for alcohol/benzole mixtures :

Alcohol. Per cent. by vol.	Benzole. Per cent. by vol.	B.Th.U. per gal.
90	10	100,000
80	20	109,487
70	30	115,347
60	40	120,217

Air for Combustion. By methods described earlier, the theoretical volume of air for the combustion of alcohol of various strengths may be calculated to be as given in Table XLIII.

TABLE XLIII

THEORETICAL AIR FOR THE COMBUSTION OF ALCOHOL

Strength.	By weight.		By volume.			
	Air per lb.	Air per gal.	Cu. ft. at 0° C.		Cu. ft. at 60° F.	
			Per lb.	Per gal.	Per lb.	Per gal.
Absolute	9·0	71·5	111·0	882·0	117·0	930·0
95 per cent.	8·48	68·2	104·5	841·0	110·0	890·0
90 „	7·75	63·2	96·0	783·0	101·5	827·0
85 „	7·21	59·5	89·4	738·5	94·5	780·5
Methylated spirit (0·820) .	8·75	71·4	108·5	885·0	113·5	930·0

All necessary data relating to the composition, physical properties, air for combustion, etc., of methylated spirit will be found in Table XL (p. 215). Attention need be directed only to the effect these various factors have on the practical application of spirit in internal combustion engines.

The *explosive range* is much greater than for benzole/air and petrol/air mixtures, which give greater " flexibility " to the engine. The *rate of flame propagation* in the mixture is much slower than in the case of other fuel mixtures, so that more uniform pressure is exerted throughout the stroke ; since combustion is more prolonged the ignition must be advanced as compared with that required for petrol or benzole, and the slow rate of propagation also indicates that a lower speed of running is required. The *calorific value of the mixture* with theoretical air is only a few per cent. lower than that for petrol/air or benzole/air mixtures.

Thermal Efficiency of Alcohol. It will be seen that the relative calorific value of petrol and alcohol per lb. is as 1·55 to 1. The thermal efficiency of an internal combustion engine is, however, largely proportional to the compression, and here the high compression which is possible with alcohol without fear of pre-ignition gives it a marked advantage; so great, indeed, that the difference of their calorific values is largely eliminated. A good petrol engine will give about 20 per cent. mechanical efficiency; many Continental makers of alcohol engines will guarantee an efficiency of 30 per cent. It will be seen that the product of calorific value and mechanical efficiency in the case of these two fuels is approximately the same; indeed, the approximate relative efficiencies of engines of suitable design in each case, running respectively on benzole, petrol, and alcohol, conform to the ratios 1·1 : 1·0 : 0·9.

In the United States tests, with engines in each case working under the best conditions, very high efficiencies were obtained; with alcohol 39 per cent.; with petrol 26 per cent.; the approximate ratios therefore were 1·5 : 1.

Ricardo (*loc. cit.*) has determined the "highest useful compression ratio" for petrols, benzole, and alcohol in the variable compression engine, and the following is a summary of his results:

Fuel.	Highest useful compression ratio.	Corresponding indicated thermal efficiency.	Minimum consumption at H. U. C. R. Pints per B.H.P. hour.
Petrols	4·55/1 to 6·0/1	30·2 to 34·9	0·402 to 0·484
Benzene (98 per cent.) .	6·9/1	37·2	0·355
Alcohol (98 per cent.) .	7·5/1[1]	40·4	0·533
Methylated spirits . .	6·5/1[1]	38·5	0·609

[1] With alcohol fuels the limit was not actually reached, but Ricardo regards these figures as the useful practical limit.

Corrosion with Alcohol. One of the troubles which have arisen with alcohol in engines has been that of corrosion of valves, etc., due to the production of acid bodies. The partial oxidation of an alcohol takes place at a low temperature, and leads first to the formation of *aldehydes*, and these in turn become acids. Thus—

$$\begin{array}{ccccc} \text{Methyl alcohol} & & \text{Formaldehyde} & & \text{Formic acid} \\ CH_3.OH & \rightarrow & H.COH & \rightarrow & H.COOH \end{array}$$

$$\begin{array}{ccccc} \text{Ethyl alcohol} & & \text{Acetaldehyde} & & \text{Acetic acid} \\ C_2H_5.OH & \rightarrow & CH_3.OOH & \rightarrow & CH_3.COOH \end{array}$$

Sorel, in his exhaustive volume on "Carburetting and Combustion in Alcohol Engines," which should be consulted for detailed information on the whole subject concludes that methyl alcohol begins to form aldehyde at 160° C. (320° F.), whilst strong ethyl alcohol does not show the formation of acetaldehyde until a temperature of 300° C. (572° F.).

Aldehyde formation is due to incomplete combustion; given an excess of air it should not occur. With even a small deficiency at a moderate temperature some acetaldehyde and acetic acid are certain to be formed from the ethyl alcohol, and the exhaust gases are always liable to contain traces of acids. Running a few revolutions on petrol or benzole before stopping the engine is found to overcome the trouble of corrosion, and this offers no great difficulty, for in many cases such fuels are necessary for starting up. It must be remembered that while the engine is hot these acid products will not affect the metal; it is only on cooling, leading to their condensation on the surfaces, that action will be set up. For this reason the silencer generally is found to suffer most.

To neutralize the acid products which cause corrosion various basic volatile bodies, concentrated ammonia, nicotine, etc., are sometimes added in very small quantities.

Another type of corrosion is that set up by the fuel itself on tanks, piping, etc. In extensive trials of power alcohol and alcohol-benzole mixtures carried out by the London General Omnibus Company (1919), copper and iron were found to be badly attacked. By "tinning" with lead, or a lead-tin alloy, this was prevented. The action appears to be due to esters in the wood naphtha, which, on hydrolysis, give rise to traces of organic acids. It should not occur therefore with the synthetic methanol.

The addition of a small quantity (0·2–0·3 per cent.) of sodium benzoate is stated to be a preventative. Ormandy claims that corrosion does not take place if anhydrous alcohol is used.

Alcohol as a Fuel. Alone alcohol can hardly be regarded as a practicable fuel for internal combustion engines on account of cost and restrictions on production; for similar reasons its use in mixtures has been restricted. Nevertheless its possibilities have been fairly fully explored.

Large numbers of tests are available showing the results obtained with alcohol, and in Germany alcohol engines have worked with success for many years; it is, however, to the large series of trials made in the United States that reference must be made for the most exhaustive results on alcohol as a fuel.

Amongst the earliest trials which demonstrated the success of alcohol were those at Vienna, where the consumption of alcohol per

H.P. hour was 0·82 lb. and of petrol 0·75 lb. In the American trials, with engines built to give the best result with alcohol and petrol respectively, the compression for alcohol being 180 lb. and for petrol 70 lb. above atmospheric, the thermal efficiency on the I.H.P. and net heating value was for alcohol 39–40 per cent., for petrol 26–28 per cent. The actual fuel consumption was 0·7 lb. alcohol and 0·6 lb. petrol, so that for engines of the most suitable construction in each case, it was almost exactly equal by volume. Allowing for the difference in specific gravity the consumption of alcohol to petrol by weight is 1·14 : 1.

The general conclusions arrived at in these trials were:

(1) That any petrol engine of the ordinary type can be run on alcohol without any material alteration in the construction of the engine.

(2) The chief difficulties likely to be met with are in starting and supplying a sufficient quantity of the fuel.

(3) The maximum power is usually greater with alcohol, and the engines are more noiseless than with petrol.

(4) The fuel consumption per B.H.P. with a good small stationary engine may be expected to be 1 lb. (or a little over) with alcohol and 0·7 lb. with petrol.

The alcohol/air mixture burns at a slower rate than the petrol/air mixture, so that for the best results ignition must take place earlier with alcohol. In tests with a 15-H.P. petrol engine, load 85 per cent. of maximum, the best consumption of 0·66 lb. per B.H.P. hour was attained with ignition 13° before the dead centre; with alcohol, 79 per cent. load, the best consumption was 1·1 lb., with the ignition at 25°.

The effect of more or less water in the alcohol is of importance, since the economic production of cheap alcohol for fuel will be dependent to a considerable extent on the degree of freedom from water of the alcohol. The conclusion arrived at in the United States trials was that for a given engine, load and compression, the consumption of pure alcohol per B.H.P. increases with the water, and the maximum available H.P. decreases, but not to a great extent. From 80 to 94 per cent. of alcohol the consumption of *pure* alcohol is about the same, i.e. the total consumption is almost directly proportional to the increase in the percentage of water. There seems little to be gained in the way of better performance of the engine with purer alcohol, so that the extra cost involved in obtaining very low percentage of water in the alcohol is by no means commensurate with the better result it gives in practice. When, however, the alcohol is to be employed in mixture fuels the water content is of great importance.

The difficulty which arises in the use of alcohol with carburettors, due to its insufficiently high vapour pressure at normal temperatures, may be overcome by mixing with a more highly-volatile combustible such as ether. For countries where alcohol can be cheaply produced from more or less waste material, e.g. molasses, ether has a great advantage over benzole or petrol, for it, in turn, is obtained from alcohol. In South Africa a fuel containing alcohol, 60 parts; ether, 40 parts, together with a trace of ammonia, to neutralize corrosion, has been successful, whilst in Brazil a mixture of alcohol ("absolute"), 85 parts; ether, 15 parts, coloured with methyl blue has been used, and also one of 75 parts "crude" alcohol; 20 parts of ether and 5 parts of kerosine.

FUEL MIXTURES FOR INTERNAL COMBUSTION ENGINES

A large number of mixtures of the three fuels—petrol, benzole and alcohol, in some few cases other components also—have been used. Broadly, the idea has been to improve the anti-knock qualities of petrol by the addition of aromatic hydrocarbons, and, in the case of alcohol, chiefly to encourage the use of a certain amount of home-produced fuel in place of a wholly imported fuel. In addition alcohol has advantages in high-compression engines, and for this reason has been used in special fuels for racing machines.

Petrol-Benzole Mixtures. These include the "benzole mixture" widely sold in Great Britain. As mentioned previously the addition of aromatic hydrocarbons raises the "anti-knock" value; benzole has a calorific value per gallon about 9 per cent. higher than petrol. Benzole alone has too small a content of low-boiling constituents to make starting easy, especially in cold weather, and moreover too high a crystallizing-point. Blending, therefore, is advantageous for each of the liquids.

"Benzole mixtures" usually contain about 30 per cent. of motor benzole and 70 per cent. of petrol. Such a mixture is suitable for use in ordinary engines without any modification of the carburettor float or jet and has the advantage of a good anti-knock value (high octane number, p. 221).

Approximately one volume of liquid benzole requires 8 per cent. more air than petrol. If a carburettor is set to the rich mixture side for petrol, unless adjustment is made there may be such a deficiency of air with benzole mixture that some free carbon is formed, which is evidenced by a sooty deposit, and frequently soot contamination of the engine lubricating oil.

Mixtures containing less than 50 per cent. of benzole will have freezing-points well below − 15° C. (+ 5° F.). For an aircraft fuel which must not solidify above − 60° C. the British Standard Specification (in accordance with the Royal Air Force requirements) for 0·760 specific gravity fuel, must contain not less than 35 per cent. by volume of aromatic hydrocarbons, and the aromatics must therefore be mainly toluene and xylene to give this exceptionally low freezing-point.

An important point in making mixtures of benzole and petrol is the precipitation of water if the benzole contains appreciable quantities. At 10° C. 100 grams of benzole are saturated with 0·04 grams; at 20°, with 0·06 grams; at 30°, with 0·09 grams, these quantities being approximately 10 times as great as for the solubility of water in petrol.

Benzole is a component of "Power Alcohol" (p. 236).

Benzole/Alcohol Mixtures. Pure benzene and absolute alcohol mix in all proportions giving stable mixtures, but with alcohol of 95 per cent. (by vol.) strength at low temperatures separation into two phases occurs. With alcohol of the above strength (i.e. 92·3 per cent. (by weight)) if the quantity of benzene in the mixture exceeds 25 per cent. (by weight) separation occurs above − 15° C. This limits the employment of such binary mixtures to those of high alcohol content. An alcohol fuel of this type produced in Great Britain consists of alcohol (95 per cent. by vol.), 77 parts; aromatic hydrocarbons, 22·5 per cent.; other constituents, 0·5 per cent. The freezing-point is below − 30° C. The calorific values of this mixture will be found on page 236.

The blending of alcohol containing but a small percentage of water with other liquids is facilitated by the addition of one of the higher alcohols; butyl and amyl alcohols have been used for this purpose; or stable ternary mixtures of alcohol/petrol and benzene may be made. King and Manning (*J. Inst. Pet. Tech.*, 1929, **15**, 350) have published valuable data on mixtures.

The most widely investigated mixtures are those of alcohol with petrol and in some countries the use of a certain amount of alcohol with petrol is compulsory. In France three motor fuels are recognized: (1) *essence tourisme*—which may be either light petrol, or this with 11–20 per cent. of alcohol; (2) *carburant poid lourd*—a heavy petrol with 25–35 per cent. of alcohol; (3) *carburant nationale*—equal parts of light petrol and alcohol.

The petrol/alcohol fuels have been extensively investigated in the United States of America, in view of proposals to penalize other fuels not containing alcohol in the interests of agriculture.

In one series of tests extending over ninety days, in which 28,000 gals. of the mixture containing 10 per cent. of alcohol, with car speeds of 30 m.p.h., the fuel showed about 10 per cent. less mileage; one pint of commercial anti-knock petrol gave a mileage of 3·2; 60–62

U.S. petrol, 3·175; alcohol/petrol, 2·9 miles. Laboratory engine tests showed about 4 per cent. decrease in efficiency.

On the other hand, it has been claimed that German "Monopolin," 20 per cent. absolute alcohol; 80 per cent. petrol, showed a saving of 1·7 per cent. over petrol and 10 per cent. over a petrol/benzole mixture.

In tests made on a standard C.F.R. engine (p. 221) the 10 per cent. alcohol/petrol mixture gave 5 units higher octane value.

King and Manning (*J. Inst. Pet. Techs.*, 1929, **15**, 350) state that alcohol/petrol mixture (25 per cent. alcohol, 75 per cent. petrol), (*a*) cannot be used satisfactorily in a standard petrol engine; (*b*) it is difficult to start from cold, although the engine can be changed over after starting on petrol; (*c*) the range of mixture strengths over which smooth running is obtained is extremely limited, and also uneconomical; (*d*) satisfactory results would probably be obtained by a "hot spot" or re-designing the induction manifold.

TERNARY FUEL MIXTURES

Almost any combination of alcohol, benzole and petrol can be used; in all the intention is to employ as much home-produced alcohol as is economically possible, in most countries, with the direct object of assisting agriculture. A few typical examples may be quoted:

	Alcohol.	Benzole.	Other components.
Germany	50	25	25 (petrol)
„	15	35	50 (petrol)
„ Wartime	25	50	25 (tetralin)
„ „	34	57	9 (tetralin)
Britain	50	28	22 ("vaporizing" oil) with some pyridine.

An extensive series of tests were run by the London General Omnibus Company (see *Eng.*, 1920, **110**, 623) on alcohol-benzole and alcohol-benzole-ether mixtures. In a large number of bench tests the compression was 123 lb. per sq. in., and the conclusion was reached that the best results can be obtained with such slow-burning mixtures in engines with overhead valves and long stroke and high compression. In a road test, compression raised to 160 lb. per sq. in., the best result was obtained with a 70 per cent. alcohol mixture, the thermal efficiency of the mixture being over 10 per cent. better than for petrol at normal compression (about 70 lb.). A series of "service" tests with 50 per cent. mixture at 123 lb. compression gave an average of 6·05 miles per gallon compared with 7·19 miles per gallon of petrol. In an engine with normal compression tests were made on a mixture of alcohol, 65 per cent.; benzole, 30 per cent.; ether, 5 per cent. The ether enabled a cold start to be made, and the fuel behaved excellently, and consumption was very slightly higher than for petrol. In many cases a considerable quantity of naphthalene is employed, but this is not advisable, as it tends to formation of sooty deposits. It is recommended to add about 1 per cent. of lubricating oil to prevent corrosion.

" TETRALIN "

Tetrahydronaphthalene, $C_{10}H_{12}$

This liquid hydrocarbon, produced by the hydrogenation of the naphthalene ($C_{10}H_8$) abundantly present in high-temperature tars, is employed to a small extent in some blended fuels. German " Reichskaftstoff " is a mixture of benzole, 50 parts; alcohol, 25 parts; tetralin, 25 parts. The vapour pressure of tetralin is only about 0·5 mm. at 20° C., so that alone it is incapable of carburetting air.

The specific gravity is 0·975; boiling-point, 205° C.; freezing-point, – 35° C.; flash-point, 79° C. (176° F.), and the gross calorific value is 20,880 B.Th.U. per lb.

Further information regarding this substance can be found in a paper by Sir F. L. Nathan (*Fuel*, 1924, **3**, 346).

CHAPTER XII

HEAVY FUELS FOR INTERNAL COMBUSTION ENGINES

LIGHT OILS (PARAFFIN OIL, KEROSINE)

The oils so largely employed in slow-speed internal combustion engines are those sold mainly for general illuminating purposes, having a flash-point higher than 70° F., although some special oils intended for use solely in such engines are now put on the market. The usual temperature over which such oils are collected is from 150° to 300° C. (303–572° F.). The general distillation process by which these oils are obtained has been described already (p. 157).

The use of these oils for power purposes offers some advantages over petrol. They form a much higher percentage of the total distillate obtained by straight distillation from the crude oil; their flash-point is so high that less stringent precautions are required in their storage and distribution, and their average price less than that of petrol.

Having a calorific value per lb. equal to petrol, with their higher density they afford a much larger number of heat units to the gallon than does petrol, so that in suitable engines their use is very economical.

Owing to their relatively low vapour pressure it is impossible to form an explosive mixture with air in the same manner as with a petrol carburettor; heat has to be applied in order to vaporize the oil. Without special care this may lead to "cracking" of the oil, and this again to a considerable modification of the amount of air required, besides the almost certain appearance of sooty deposit. When a spray of paraffin oil is carried forward into the cylinder condensation of some portion is very likely to occur before complete combustion, and generally it is more difficult to attain that uniform composition of the mixture necessary in a high-speed engine. This uniformity is of far greater importance in a high-speed engine running on illuminating oils, because the range of explosion of the mixture is only about half that of the petrol/air mixture, which itself is a narrow one.

Petrol engines have been designed for use with illuminating oils and work successfully at nearly constant speeds, but the difficulty of maintaining the constancy of the mixture with variable speeds has practically confined the general use of these higher distillates to slow-speed engines running without those wide fluctuations which occur with the ordinary petrol engine.

Composition and Properties of Paraffin Oil. *The general character of these oils has been referred to under the composition of crude petroleum. Being higher members of homologous series of hydrocarbons their average percentage composition agrees with that of the* petrols. The composition and calorific value, determined in a bomb calorimeter by Inchley (*The Eng.*, 1911, **111**, 155) are given in Table XLIV.

TABLE XLIV

COMPOSITION AND CALORIFIC VALUE OF PARAFFIN OILS (*Inchley*)

Name.	Specific gravity	Composition.			Calories per kilo.	Calorific value.	
		Carbon.	Hydrogen.	Oxygen, Nitrogen, etc.		B.Th.U. per lb.	B.Th.U. per gal.
Royal Daylight (American) . .	0·797	85·70	14·20	—	11,167	20,100	159,000
Kerosine (American)	0·780	85·05	14·40	0·55	11,163	20,095	156,500
Refined (Baku) . .	0·825	86·00	14·00	—	11,270	20,300	167,000
Russole, R.V.O.. .	0·890	85·95	13·50	0·45	10,901	19,620	174,500
Solar Oil . . .	0·896	86·61	12·60	0·79	10,783	19,450	174,000

The following determinations (Table XLV) of calorific value (bomb calorimeter) and specific heat were made by Brame:

TABLE XLV

CALORIFIC VALUE AND SPECIFIC HEAT OF PARAFFIN OILS

Name.	Specific gravity.	Calorific value.			Specific heat.
		Calories per kilo.	B.Th.U. per lb.	B.Th.U. per gal.	
Royal Daylight (Tea Rose)	0·8055	11,100	19,980	160,500	0·450
Water White (White Rose)	0·800	11,140	20,050	160,400	0·457
Russian	0·8248	11,060	19,910	164,000	0·435
Roumanian	0·8127	10,900	19,620	159,500	0·444

The flash-point of these oils is seldom below 81° F.; that of the special engine fuels (Russolene, "R.V.O.," etc.) is generally from 82–86° F.

The earlier oil engines were developed mainly with American oils of about sp. gr. 0·80 as the fuel. With the introduction of the heavier Russian oils, sp. gr. 0·84, the results obtained were not so good. It was found, however, that by a slight increase of compression, by means of a plate fixed on the piston, and frequently increasing the proportion of air, the engine output was often considerably increased with the heavier Russian oils. This variation in conditions necessary to ensure the best results has led to a careful standardization of oils suitable for engines of this type.

Consumption of Oil. Under test conditions at full load the consumption of oil of the above description has frequently not exceeded 0·6 lb. per B.H.P. hour. With a specific gravity of 0·80 the pint of oil would weigh one pound, so that the consumption in pints is practically synonymous with the consumption in pounds. Under everyday running conditions at anything closely approaching full load an average consumption of oil of good quality may be taken as 0·70 lb. (or pints).

The thermal efficiency of this type of engine is between 21 and 22 per cent.

HEAVY OILS FOR COMPRESSION-IGNITION ENGINES

In this class are included those oils suitable for Diesel-type and the so-called semi-Diesel-type engines, both of which are acquiring more and more importance. Large numbers of ships are already fitted with Diesel-type engines, and the number is being added to yearly in the mercantile marine of all countries. For auxiliary machinery in battleships and as the main engines in submarines they are also of importance. For such purposes, where continued running without trouble over long periods is essential, the suitability of the fuel is a matter of primary importance.

Of recent years there has been a great development of high-speed engines of the Diesel type, which has made them applicable to motorbuses, heavy commercial vehicles, and aircraft engines.

In both types of engine the fuel is injected as a spray at about the end of the compression stroke, the air alone being compressed. In engines of the Diesel type this compression, to 450–550 lb. per square in., raises the temperature of the air to about 550°–650° C., which ensures spontaneous ignition of most of the fuels employed. In semi-Diesel-type engines the air is compressed only to about half this pressure, and ignition is dependent largely upon some such device as a heated bulb in connection with the cylinder, and into which the fuel spray is forced.

Since in neither type of engine is ignition dependent on any flame or spark (except in some cases a heater of some sort for starting), they are now generally known as "*compression-ignition*" engines.

For the semi-Diesel or "hot-bulb" type of engine a moderately heavy petroleum distillate is the most suitable fuel. Frequently these engines are referred to as "crude oil" engines—a misnomer, for crude oil is practically never employed.

Diesel-type engines are capable of working with almost any combustible liquid providing it has certain ignition characteristics and not too high a volatility, as this is liable to produce uneven running. The highest grade "Diesel oil" is the fraction of crude petroleum intermediate between kerosine and the heavier lubricating oils (roughly corresponding to gas oil, or Solar or "intermediate" oil, p. 158). Petroleum residue oils (as distinct from distillates) may be used, providing they are reasonably free from asphaltum. Shale oil, particularly the "intermediate" oil, is also an excellent fuel, being free from asphaltum. Tar oils (from lignite, coal, etc.), and in some cases even crude low-temperature tar, are used, and vegetable oils, such as palm oil and arachis oil, have proved good fuels, but can hardly be regarded as having commercial possibilities, except perhaps in the producing area.

Properties of Compression-Ignition Engine Oils.

Ignition Temperature and Ignition Delay. Obviously the Spontaneous Ignition Temperature (S.I.T.) must be sufficiently below the temperature of compression to ensure the fuel igniting even with a cold start; with the larger slow-speed engines no other means of ignition beyond compression of the air is required, but for the smaller high-speed engines it is frequently the practice to instal an electric resistance heater, which is cut out when the engine begins to function, or other form of igniter.

It is frequently stated that the temperature of spontaneous ignition is related, broadly, to the hydrogen content. Rieppel has suggested that those oils which ignite well owe this property to their "cracking" at the temperature of the compressed air; they thus set free hydrogen and form heavier hydrocarbons, the low ignition point of the hydrogen initiating the combustion by which the whole of the heavier residues ultimately become consumed. Allner considers that ethylene is a product of the cracking and that ignition is brought about by this hydrocarbon, the ignition point of which is 542–547° C. With the other class of fuels this cracking is absent, and though the more volatile portions doubtless vaporize, the ignition is not satisfactory, and they are either not properly consumed or burn with explosive force.

For testing the S.I.T. of compression-ignition fuels under practical conditions a special apparatus has been designed at the Air Ministry Experimental Station, Farnborough, and this has been described by Foord (*J. Inst. Pet. Tech.*, 1932, **18**, 533).

Another factor is, however, of primary importance, namely the "delay period" or "lag"—the time interval between the opening of the fuel valve and the first rise of pressure, due to combustion. If much fuel is in the cylinder before proper ignition—and this depends on the delay time—the greater will be the "shock pressure." According to Boerlage and Broeze (*J.S.A.E.*, 1932, **31**, 283), the delay period governs the roughness of running, ignition, production of smoke and offensive exhaust, and in some cases piston gumming. They consider that fuels which crack easily have the better ignition qualities, ignition being in the first place due to the radicals resulting from cracking combining with oxygen.

Broadly, the characters of fuels best suited to compression-ignition engines are the opposite of those desirable in petrol engines, and just as it has been found of great service to rate the latter on their octane numbers (p. 221), Boerlage and Broeze proposed to use cetene ($C_{16}H_{32}$) as a standard for a "*cetene number*" for compression-ignition fuels. This hydrocarbon has very high ignition characters; on the other hand, α-methylnaphthalene does not ignite in a normal compression-ignition engine. By using mixtures of these two as primary standards the relative ignition characters of a fuel may be expressed as the cetene number—the percentage by volume of cetene in the mixture which has the same ignition quality as the fuel.

The cetene number determination requires that specially designed engines are available; where they are not an alternative of considerable service is found in the "aniline point" of the fuel. This is the temperature at which equal volumes of dry re-distilled aniline and the fuel cease to be completely miscible—that is become cloudy on cooling. There is a fairly good relationship between this "aniline point" and the "cetene number" for most petroleum fuels, but this does not hold for coal tar oils and is doubtful for some shale oils. Approximately the aniline point should be not less than 65° C., a temperature corresponding to a cetene number of about 55.

Le Mesurier and Stansfield (*J. Inst. Pet. Tech.*, 1931, **17**, 387) state that from running tests a low cetene value may be 42, whilst a high-standard fuel may have a value of 69, and the difference between a poor fuel and a good one may therefore be some 30 cetene numbers.

Delay time is a function of temperature; as would be expected, increase of temperature shortens the time.

Viscosity. The rate of burning and completeness of combustion are largely dependent on the fineness of the mist of injected oil, and this in turn, for given pressure and temperature conditions with any one injector, on the viscosity of the fuel as injected. The viscosity is in turn largely dependent on composition, asphaltic oils and crude tars being viscous. It is more difficult to burn these completely because of the greater difficulty in getting a fine spray, and because asphalt and the pitch of tars are slow burning and form coke in the cylinders. Two of the most important tests applied to fuels for engines of either of the types are therefore the estimation of the *asphalt content* and the liability to form coke (*coking test*).

The *flash-point* should not be too low; it is indicative of volatility, and, as previously mentioned, too high volatility is not desirable. Further oils for such engines will usually have to comply with the regulations, which generally demand a minimum flash-point of 150° F. for fuel oils.

Mineral matter (*ash*) should be practically absent; a hard ash causes excessive wear in cylinders and pistons by abrasion. As high compressions have to be maintained for successful running, this question of wear is most important.

Asphalt is a very indefinite material. Two main kinds are recognized, "hard asphalt," which is insoluble in petroleum spirit boiling between 60° and 80° C.; "soft asphalt," which is precipitated from an ether solution of the oil by the addition of alcohol. Broadly, asphalt is undesirable in oils for internal combustion engines, but soft asphalt is not nearly so objectionable as hard asphalt. Diesel engines have been run successfully for considerable periods on oils containing a fairly high percentage of soft asphalt.

The *cold test* should be low enough to ensure that no separation of wax is likely at the lowest temperature the oil may reach.

Distillate oils are naturally free from all but traces of asphalt, mineral matter, etc., and give a low coking test. They therefore form the best type of fuel for Diesel and semi-Diesel engines.

Large engines have been run for long periods on oils containing up to 2 per cent. of hard asphalt, but, according to Le Mesurier and Stansfield (*Inst. Marine Eng.*, 1934, *46*, 129), for small high-speed engines, with limited combustion chamber volume, in which the time available for combustion is short, oils containing more than about 0·1 per cent. of hard asphalt are not to be recommended. In general, this means the use of distillate oils.

Residue oils, on the other hand, are more widely obtainable and less costly. Providing that they are not too viscous, not too high in asphalt and ash content, they form very serviceable fuels for slow-speed compression-ignition engines. It is a common practice to put such fuels through a high-speed centrifuge before injection, and this removes practically all water, sediment, and abrasive ash, so reducing cylinder wear.

Distillation tests are of little importance with heavier compression-ignition engine fuels, though for the lighter fuels for high-speed engines, such as aircraft, they are of value. Le Mesurier states that indicator diagrams are more erratic when the fuel has a wide distillation range, and further that highly naphthenic oils are more liable to "shocks" in running. According to U.S. Bureau of Mines Technical Paper No

37 (1913), in which the requirements of Diesel fuels are very fully set out, 80 per cent. of the fuel should distil below 350° C.; oils having more than 20 per cent. residue showing large carbon residue on coking. This, however, must largely depend on the composition of the oil.

Specifications. The British Standards specifications (209, 1924) demand a fuel wholly of petroleum or shale oil origin. This ensures a satisfactory calorific value (18,500–19,000 B.Th.U. *gross* per lb.). Four grades—determined mainly by the hard asphalt content—have been adopted, the asphalt limits being: Grade No. 1, 0·5; No. 2, 2·0; No. 3, 4·0; No. 4, 12·0 per cent.

The *ash content* of the highest grade (No. 1) must be below 0·01 per cent.; for the other grades 0·05 per cent.

The *water content* of Grade No. 1 must not exceed 0·5 per cent.; for the other grades 1 per cent.

The *viscosity*, determined in a Redwood No. 1 Viscometer at 100° F. must not exceed: Grade No. 1, 75 sec.; No. 2, 250 sec.; No. 3, 750 sec.; No. 4, 1500 sec., for 50 c.c. of oil.

The *cold test* requires the oil to remain liquid at the following temperatures: Grade No. 1, 20° F.; No. 2, 35° F.; No. 3, 40° F.; No. 4, 45° F.

An Admiralty specification requires the oil to be either a shale oil or a distillate of petroleum, with a flash-point not below 175° F. (closed test), a cold test of 20° F., acidity not to exceed 10 mgm. of potassium hydroxide per 100 grams of oil; water not to exceed 0·5 per cent.; hard asphalt, 0·1 per cent.; ash, 0·01 per cent.

The following are specifications suggested by the special Research Committee of the American Society of Mechanical Engineers:

	Heavy duty engines.	Light high-speed engines.
Viscosity at 100° F. (Redwood Secs.)[1]	Max. 200	Min. 41 Max. 85
Sulphur	Max. 3·0 per cent.	Max. 2·0 per cent.
Ash	„ 0·08 „	„ 0·02 „
Conradson Coke Test	„ 4·0 „	„ 1·0 „
Water and Sediment	„ 1·0 „	„ 0·5 „
Flash-point	Min. 150° F.	Min. 150° F.

[1] Figures converted from Saybolt Universal.

A very complete record of a "contract" oil has been published by Michler:

Specific gravity. . .	0·904	Ash . . . . below	0·05 per cent.
Flash-point (P.M.) above	150° F.	Water . . . . „	0·50 „
Viscosity, 100° F. Redwood	85 sec.	Hydrogen not less than	11·0 „
Hard asphalt . below	1·0 per cent.	Carbon . „ „	86·0 „
Coke . . . . „	1·5 „	Sulphur. . . below	1·0 „

Tars and Tar Oils. Very little tar, other than coal tar, is available as fuel. Lignite tars are produced in fair quantity on the Continent and are more or less intermediate in character between petroleum and coal tar; they usually contain a high proportion of paraffin wax.

The character of coal tar is very largely dependent upon the temperature and conditions of carbonization. This question has been discussed in a previous section. Broadly, the high-temperature tars from horizontal retorts contain so much pitch, free carbon, ash, etc., and are so viscid that such tars are unusable as fuels for Diesel engines. Low-temperature tars have, however, proved less unsuitable.

In general, however, distillates from the crude tars are employed. These are known as "tar oils," and although they contain considerable quantities of naphthalene, which may crystallize out at moderately low temperatures and cause difficulty, are practically free from pitch, "free carbon," and ash. The "tar oils" have consequently proved much more satisfactory than crude tars. The tar oils are derived from the carbolic, creosote, and anthracene oil fractions from the distillation of the tar; although much of the tar acids (phenols) will be removed from the carbolic oil fraction, yet a considerable percentage of acids remain. With low-temperature tars the tar acids are high. They lower the calorific value and so increase the fuel consumption, and Ban and Suwa state that under light loads they give rise to misfiring and detonation, and in order to produce a satisfactory compression-ignition oil from low-temperature tar, the tar acids should be removed. Other independent tests confirm that they cause rough running.

Some use has been made of the lower-boiling parts of the creosote oil fraction of coal tar in spark-ignition internal combustion engines, but the results have not fulfilled expectations. A report on these fuels has been submitted by H. M. Spiers and E. W. Smith to the Institute of Gas Engineers (Nov., 1934).

The distillation range of the light creosote oil is from about 150°–270° C., and this determines the use of petrol for heating up the engine in the first place and special heating arrangements for the induction manifold. The light creosote is not used alone, a proportion of benzole or "white solvent naphtha" is added, the ratio being respectively about 90/10.

The normal creosote contains a high percentage of tar acids, and most of these have to be removed by soda washing, usually followed by distillation; a small portion not removed helps to keep naphthalene in solution at low temperatures, benzole and naphtha having a similar action. The more completely the tar acids are removed the greater the quantity of naphtha required.

Very different opinions on the results of the trials have been recorded. Public service vehicles have been run mainly on this fuel mixture, but in the case of the pioneer concern after two years its use has been abandoned. Costs of maintenance have been increased in cases owing to more mechanical troubles. One important point has been lubrication. Owing to the high-boiling range of the fuel, crank case dilution is much greater than with petrol, from 9 to 30 per cent. dilution being recorded. Most mineral oils have, in addition, given bad sludges and had to be frequently changed. Castor oil has proved the most successful lubricant.

For compression-ignition engines one very important consideration is the spontaneous ignition temperature of tars and tar oils. This is considerably higher than that of petroleum oils. Moore (*J.S.C.I.*, 1917, **36**, 109) gives the following figures for ignition in *oxygen*: heavy petroleum fuel oils, about 260° C.; creosote oil, 415° C.; coke-oven tar oil, 478° C.; low-temperature tar, 307° C.

Whilst Diesel engines which have been warmed up on petroleum oils have been run on tar oils, without alteration beyond advancing the fuel admission, at loads of 75 per cent. of the full load, or above, in general the temperatures reached by compression of the air are not sufficiently high. There are good mechanical reasons for not increasing the compressions further; an undue amount of petroleum oil has to be mixed with tar oils to give certain ignition (admixture of petroleum oil with tars almost invariably leads to precipitation of heavy pitch-like material), so the procedure for running Diesel engines on tar oil, which was made compulsory during the war owing to shortage of petroleum fuels, was to use a small quantity of petroleum oil as "ignition oil," this being injected into the cylinder by a special pump through a separate valve to the main charge of tar oil.

The quantity of ignition oil varied with the age of the engine and load; from data obtained at various loads the ignition oil at full load was usually about 10 per cent. of the total fuel, although in new engines it was somewhat less.

Trouble through choking of passages in the fuel admission system was not infrequent and necessitated stoppages for clearing. Turnbull recommended making a short run every five hours on petroleum oil, by which means some three hundred hours' continuous running was possible.

It must be remembered that although the widest experience in the use of tar oils in Diesel engines was gained during the war period, it was with oils from high-temperature tar. Naphthalene separation was one difficulty which had to be guarded against and often necessitated arrangements for heating the tar oils to prevent separation. One leading Continental firm of engine makers required that no separation of solids should occur in thirty minutes at 46° F.

The following are the usually accepted limits for "tar oil" fuels: material insoluble in xylol ("free carbon," etc.), 0·2 per cent.; ash, 0·05 per cent.; carbon residue, below 3 per cent.

In the Report of the Director of Fuel Research (1926) it is stated that attempts to run a Diesel engine on the heavier fractions from low-temperature tar had been unsuccessful, owing chiefly to detonations, but a mixture with 20 per cent. light American fuel oil gave no difficulty. A peat tar was also used, and, observing special precautions in starting and fuel injection, the maximum power output was 90 per cent. of the standard. fuel.

In the D.F.R. Report (1928) it was stated that a suitable Diesel fuel had been obtained in the distillate boiling between 200° and 350° C. from low-temperature tar. With normal spray valves this fuel had shown a tendency to give delayed ignition, followed by heavy detonation, but it was expected that an improved type of injection would enable better results to be obtained. By blending one part of this tar oil with four parts of shale oil a satisfactory fuel was obtained. It could hardly be described as a tar oil fuel. In the same report it is mentioned that at the Admiralty Engineering Research Laboratory a suitable form of valve had been evolved for use with tar oil alone and no difficulty had been experienced with choked fuel valves or carbon deposit. Consumptions of tar oil and petroleum oils were practically in the inverse ratio of their calorific values.

It may be said generally, therefore, that tar oils can be made suitable for the slow-speed Diesel engine where a high ignition temperature is not very important. Le Mesurier and Stansfield (*J. Inst. Pet. Tech.*, 1931, **17**, 388) have compared the behaviour of a number of tar oils having ignition temperatures over 520° C., and state that, while suitable for slow-speed engines, considerable modification would be necessary to suit them for the high-speed engine. The following expedients can be adopted: (i) pilot ignition, (ii) a good starting fuel, (iii) blending with other oils and (iv) " dopes." The most attractive of these is the use of dopes or pro-knock substances. A cheap material is not yet available, but it has been shown that the idea is sound. For example, the addition of 2·5 per cent. of ethyl nitrate has a large effect on both ignition temperature and ignition lag; the former being reduced in the case of fuel oil, from 325° to 300° C., and the latter from 0·6 to 0·1 sec. at 400° C. It is to be hoped either that cheaper dopes can be found or that suitable changes can be made in the engine design to cope with fuels of this type.

Consumption of Petroleum Oils and Tars. The consumption of heavy petroleum oils in the Diesel engine is from 0·40–0·45 lb. per B.H.P. hour; with tar oils the consumption is from 0·48–0·50 lb., together with 0·01–0·02 lb. of petroleum ignition oil.

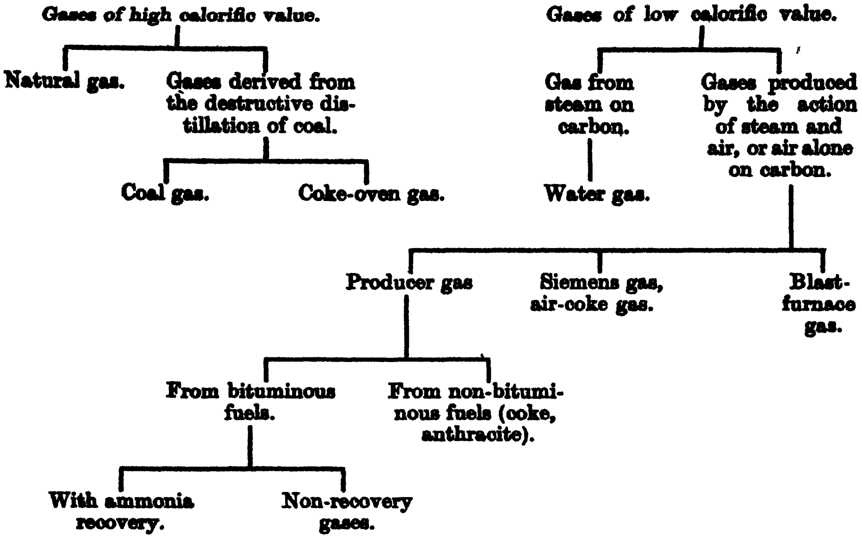
The widest experience with compression-ignition engines has probably been in electric generating stations. In a comparative trial of petroleum fuel and tar oils " under test " conditions the former showed a consumption of 0·65 lb. and the latter 0·735 lb. per unit generated.

The Diesel Engine Users' Association publish valuable data on fuel consumptions, running costs, etc. In the Report (1934) the average fuel (petroleum oil) per unit generated is given as 0·648 lb., under an average load factor of 67·2 per cent. From the data for the large number of stations included 0·59 lb. may be taken as a very good consumption figure.

According to Clarke, the air necessary for proper combustion in the Diesel engine is 3·3 times the theoretical. The theoretical volume at 60° F. would be approximately 190 cu. ft. per lb., so that, on Clarke's estimate, some 630 cu. ft. of air are actually required. It is evident that the heat losses in the exhaust gases with such a large mass of air will be very high.

The consumption in crude oil engines of the semi-Diesel type is about 0·55–0·6 pint per B.H.P. hour. With a sp. gr. of 0·9 this is equal to 0·62–0·67 lb.

CLASSIFICATION OF GASEOUS FUELS


Gases of high calorific value.
Natural gas.
Gases derived from the destructive distillation of coal.
Coal gas.
Coke-oven gas.
Gases of low calorific value.
Gas from steam on carbon.
Water gas.
Gases produced by the action of steam and air, or air alone on carbon.
Producer gas
Siemens gas, air-coke gas.
Blast-furnace gas.
From bituminous fuels.
From non-bituminous fuels (coke, anthracite).
With ammonia recovery.
Non-recovery gases.

NATURAL GAS

Enormous quantities of "natural gas" are produced in many countries where petroleum is found, and although there is still great wastage, the quantities made use of run into billions of cubic feet annually. Much is used for heating, both industrial and domestic, and large quantities are treated for the recovery of natural gas "gasoline" (p. 209).

The gas actually utilized reached a peak production in the United States in 1920, but little short of 2,000,000 million cu. ft.; Roumania, 63,000 million (1932) and Canada, 29,376 million cu. ft. (1930). In this country small quantities are produced at Heathfield, amounting to about 7 million cu. ft. annually, and is distributed for heating and lighting in the immediate neighbourhood. Gas is also found at Ruabon, North Wales.

Composition and Calorific Value. These vary over wide limits not only in different localities, but also from the same boring at different periods. The percentage of saturated hydrocarbons, principally methane (CH_4), is always high; in a large number of cases over 90 per cent. Hydrogen is present usually to the extent of 1 to 2 per cent., though in some few cases the amount has exceeded 20 per cent. The other combustible gases present in small amounts are ethane, unsaturated hydrocarbons and carbon monoxide.

Owing to the high calorific value of the saturated hydrocarbons and the small percentage of non-combustible gases present, natural gas has a correspondingly high thermal value. The following analyses may be taken as typical:

	Alabama.	California.	Kansas.	Illinois.
Methane	97·6	77·5	62·2	37·5
Ethane	—	16·0	18·4	59·6
Carbon dioxide	0·3	6·5	—	—
Nitrogen	2·1	—	18·6	1·7
B.Th.U. per cu. ft. at 0° C. and 760 mm. Gross	1039	1123	930	1590

After gas has been evolved from a boring for some time its composition changes, the proportion of paraffin hydrocarbons of higher molecular weight increasing.

"Casing-head" gasoline is produced from natural gas by special means involving either absorption in wash-oil or active charcoal or by compressing the cooled gas (p. 209), when liquids separate. Being of lower boiling range, this gasoline is of value for blending with motor spirit. Removal of the gasoline reduces the calorific value of the gas from say 1140 to 900 B.Th.U. per cu. ft. The annual production of casing-head gasoline in the United States is over 500 million gallons.

COAL GAS

The use of coal gas was confined for the greater part of a century to purposes of illumination; the development of the gas engine and its great increase in thermal efficiency subsequently rendered coal gas an important power-producing fuel, and with its extended use for domestic heating purposes, and still more recently, with cheaper rates and highly efficient methods of combustion, it has become an important fuel in many manufacturing operations, such as metal melting, annealing, etc., all contributing to the further and extended use of this efficient and convenient form of gaseous fuel.

The main important features which contribute to the successful commercial application of coal gas are—the constancy of supply of fuel of uniform composition, available at any moment, the avoidance of all stand-by costs, the high thermal value and high efficiency which can be obtained in engines or suitable furnaces, and in most cases in industrial centres the comparatively low cost per thousand cubic feet. Naturally costs vary over very wide limits, and the question as to whether coal gas is the most economical fuel must depend largely upon costs and quantity consumed, but as the price of gas must be very largely dependent on the price of coal, the issue of cost between the two fuels naturally remains much in the same position. The extended use of coal gas, other than for illumination, has had an important influence on the "load factor" at many works; it is not unusual to have a day demand of nearly 50 per cent. of the night consumption. This levelling up of the day and night load factor makes for considerable economy in production.

The quantity of coal carbonized and the gas produced in the United Kingdom increased steadily for many years, but more recently, as the following figures show, there has been some decline.

	1931.	1933.	
Coal carbonized	18,145,000	16,714,000	tons
Oil for carburetted water gas	53,124,000	53,124,000	gals.
Total gas made	315,570	309,560	million cu. ft.
Coal gas	254,350	249,180	
Water gas	40,800	39,240	
Coke sold	7,672,000	7,115,490	tons
Coke breeze sold	528,000	500,000	tons
Tar	212,682,000	209,983,000	gals.
Ammonium sulphate	103,000	65,830	tons

Coal gas is considered here entirely as a commercial fuel for power purposes and industrial heating. Its use for illuminating purposes is clearly outside the scope of the work; neither is it proposed to deal with the question of its use for domestic heating, etc. The reader may be referred to the reports of the Gas Investigation Committee of the Institution of Gas Engineers.

Production of Coal Gas. Space does not permit and neither is it necessary to enter into detail of the manufacture of coal gas, since such information is already fully dealt with in many excellent treatises devoted entirely to the subject. From the consumer's point of view coal gas may be taken as a "ready made" fuel, and only brief reference to some conditions of production as affecting the character of the products is required.

Coal gas is made principally in two types of retort, horizontal intermittent and vertical continuous, the former being the modernized version of the same system upon which coal gas was first made. Twelve to fourteen hundredweight charges of coal are carbonized at flue temperatures of 1350–1400° C., and thermal economies are effected by regenerative systems. Owing to these high temperatures the yield of gas is as high as possible and excessive "cracking" makes the tar low in yield and high in free carbon (see p. 164). In the other system coal is passed continuously downwards through the heated retort and the coke discharged at the bottom. Owing to this continuous treatment the gas is of uniform composition as distinct from that from horizontal retorts where uniformity is obtained only by mixing the gas from a bench containing a number of retorts. In vertical retorts steam is generally introduced at the bottom and the yield of gas is increased by the formation of water gas from the hot coke. Vertical retort gas is therefore of lower calorific value and higher specific gravity than horizontal retort gas. The tar is less cracked, is of lower specific gravity, contains less free carbon, and is produced in higher yield.

Within the last few years there has been introduced a new type of retort, i.e. the chamber oven, resembling a coke oven of small size. These ovens carbonize static charges of about 2½ tons, and the yield of gas is augmented in the final stages of carbonization by steaming the charge to produce water gas.

Coal gas supplies are augmented by the production of carburetted water gas. The calorific value of this gas can be controlled by varying the proportion of oil supplied to the carburettor per 1000 cu. ft. of water gas made (see p. 299).

Composition of Coal Gas. The following analyses of coal gases are typical of those produced in the different retorting systems referred to above. Attention is drawn to the variable nature of horizontal-retort gas by including analyses of the gas produced from a 12-cwt. charge carbonized for twelve hours.

TABLE XLVI

TYPICAL ANALYSES OF COAL GASES

Gas.	B.Th.U.	CO_2.	C_nH_m.	O_2.	CO.	H_2.	C_nH_{2n+2}.	N_2.	n^1.
Horizontal retort—									
Average	566	1·6	3·0	0·3	6·9	52·9	30·2	5·1	1·08
First hour . . .	750	2·0	6·5	0·4	7·8	38·6	40·7	4·0	—
Fourth hour . . .	580	1·4	1·0	0·4	6·4	58·8	27·3	4·1	—
Eighth hour . . .	380	1·0	*nil*	0·2	11·4	69·3	5·5	12·6	—
Vertical retort gas (10% steam)	500	2·5	1·8	0·5	15·6	57·2	17·9	4·5	1·15
Carburetted water gas	500	5·6	7·0	0·4	30·5	37·0	14·0	5·5	1·10
Chamber-oven gas .	553	1·8	3·2	0·2	10·3	55·5	25·0	4·0	1·06
Horizontal retort—									
First hour . . .	—	2·0	6·5	0·4	7·8	38·6	40·7	4·0	not stated
Second hour . . .	—	1·8	4·3	0·2	6·0	45·6	37·4	4·7	
Third hour . . .	—	1·6	2·5	0·2	6·2	53·8	32·2	3·5	
Fifth hour . . .	—	1·2	2·6	0·4	6·4	63·5	21·7	6·4	
Eighth hour . . .	—	1·0	—	0·2	11·4	69·3	5·5	12·6	
Average	566	1·6	3·0	0·3	6·9	52·9	30·2	5·1	

(Evans, *Proc. Roy. Soc. Arts*, 1924, Cantor Lectures)

The unsaturated hydrocarbons (CnHm) consist mainly of benzene vapour, ethylene, propylene and butylene, and have a mean calorific value of 2300 B.Th.U. per cu. ft. in high-temperature coal gases.

The carbon monoxide in coal gas is an undesirable constituent owing to its poisonous character, but the proportion is not limited. A Board of Trade Committee of 1922 did not recommend its limitation but insisted upon careful supervision and inspection of gas appliances.

The saturated hydrocarbons in coal gas consist mainly of the first member of the series, methane, but small quantities of ethane and less of butane are usually present. Their presence is indicated by the "*n*" value being greater than 1·0.

In addition to these constituents coal gas contains certain impurities from which it must be purified before admission into the mains. The chief impurities are the sulphur compounds (H_2S, CS_2, etc.), naphthalene and ammonia. For purified towns' gas the legal limit for sulphur compounds is 20 grains of S. per 100 cu. ft. of gas. Even traces of sulphur compounds are troublesome in gas since these form oxides of sulphur on combustion which, in combination with atmospheric or other moisture, have a strong corrosive action on metals.

Calorific Value. The standard of manufacture of coal gas is now, by the Gas Regulation Act of 1920, its calorific value, and gas is sold on a thermal basis. Each gas undertaking works to a declared calorific value, chosen by itself, and submits its accounts in units of "therms," i.e. 100,000 B.Th.U. To-day the system amounts to multiplying the gas volume supplied by its calorific value, but when a satisfactory recording calorimeter is adopted the actual average calorific value of the gas may replace the "declared" value. The consumer is, however, safeguarded because official testing ensures that the standard declared value is maintained. The value of this system of charging is potential rather than actual, for it will enable the manufacturer to adopt the most economical process of production.

COKE-OVEN GAS

Since the treatment of coal in a coke oven does not differ essentially from that in a modern horizontal gas retort, the normal coke-oven gas closely resembles horizontal-retort gas.

The economic utilization of coke-oven gas has always been difficult owing to the necessity for ensuring uniformity of calorific value for sale purposes and in arranging for distribution. Owing to the gradual perfecting of thermal recovery arrangements, and particularly of regeneration of heat in firing the ovens, a large proportion of the gas now remains for sale. In Germany and in the United States coke-oven gas has become the main source of towns' gas and a move in the same direction has been made in Yorkshire by the inception of the "gas grid" (see p. 140). The importance of utilizing this product is obvious in relation to its effect on coal consumption. With such a system as the gas grid in operation, the whole of the gas made in coke manufacture could be utilized, the gas necessary for heating the ovens being manufactured (producer gas) from the coke breeze produced. In addition a proportion of the extra capital charges caused by having stand-by plants at every works could be avoided.

In the waste-heat type of coke oven the ovens are heated by the gas produced, fuel economy being effected by heat interchange. In the regenerative systems some part of the heat is replaced by low-grade fuel. In the former case the amount of surplus gas available for sale is less than 10 per cent. of the amount made while in the latter case it may be as high as 30 per cent. In recent years the use of regenerative systems has been definitely increasing.

An overall figure of the surplus gas available may be taken as 4000 cu. ft. per ton of coal, but much of this gas may be used in other parts of the works, e.g. for tar distillation, so that the amount available for sale may be considerably less than this, about 1500 cu. ft. It is estimated that in 1931 almost 40 million cu. ft. of coke-oven gas was sold for fuel purposes, and 14 million of this by gas undertakings.

The yields of by-products from coke manufacture can be averaged as follows:

Gas	11,000 cu. ft. of 500–550 B.Th.U.
Tar	8–9 gallons
Benzole	2½ „
Sulphate of ammonia	22–30 lb.

Composition of Coke-Oven Gas. A number of analyses of the gas produced in modern ovens are given in Table XLVII. It will be seen that in some cases the evidence of air-intake is shown by the rather high percentage of nitrogen and the formation of carbon monoxide by the

TABLE XLVII

Composition of Coke-Oven Gas

Reference.	Koppers' by-product ovens.		Semet-Solvay recup.	Simon-Carves horizontal flue.	Otto-Hilgenstock vertical flue.
	Straight.	Debenzolised.			
Carbon dioxide . . .	2·2	2·2	2·3	2·9	1·7
Unsat. hydrocarbons .	3·5	2·6	3·4	2·8	2·7
Oxygen	0·3	0·3	0·4	0·3	0·4
Carbon monoxide . .	6·8	6·9	6·0	7·3	5·6
Hydrogen	47·3	47·8	46·7	48·5	55·5
Methane, ethane, etc. .	33·9	34·2	34·3	30·7	30·6
Nitrogen	6·0	6·0	5·9	7·5	3·5
B.Th.U. per cu. ft., gross	591	562	590	550	566
S.G. (air = 1) . . .	0·44	0·42	0·44	0·41	0·39

action of the air on the red-hot carbon. In many older forms of oven the hydrocarbon gases are broken down by overheating, leading to low percentage of unsaturated hydrocarbons and methane, hence poorer gas. With the most recent forms of ovens, both these causes of deterioration of the gas are avoided, and it will be seen that the gas does not differ appreciably from that produced in horizontal gas retorts.

In the distillation of large masses of coal, the penetration of heat throughout the mass is slow, and the gases escaping through cool portions of the mass exhibit necessarily all the characters of coal gas distilled at very low temperatures. As the mass cokes through, the latter portions of the gas necessarily change their character and become very poor in hydrocarbons, rich in hydrogen, and consequently of lower illuminating and calorific value. The following table (XLVIII) shows how the composition of the gases varies from beginning to end of a coking period of twenty-seven hours. The large change from a maximum of over 570 to a minimum of 254 B.Th.U. per cu. ft. shows that great care will have to be taken, when distributing coke-oven gas for sale, to ensure the necessary uniformity of composition and calorific value.

TABLE XLVIII

COMPOSITION OF COKE-OVEN GAS AT DIFFERENT PERIODS OF CARBONIZATION (Porter, "Coal Carbonization," 1924).

Hours after charging.	2.	5.	10.	15.	21.	25.	27.
Carbon dioxide	3·3	2·5	2·3	1·9	1·1	0·7	1·0
Unsat. hydrocarbons . .	5·8	4·3	2·1	2·1	1·0	0·3	0·3
Oxygen	1·0	0·6	0·2	0·1	—	0·1	0·3
Carbon monoxide . . .	0·9	2·8	2·8	3·9	4·0	4·9	4·2
Hydrogen	36·7	47·8	47·1	53·4	59·0	67·0	70·0
Saturated hydrocarbons .	42·5	34·5	31·2	33·2	21·1	12·2	4·7
Nitrogen	10·0	7·5	14·3	5·4	13·8	14·8	17·9
B.Th.U. per cu. ft. . . .	567	530	502	490	470	310	254

It will be seen that the gas produced in the last stages of carbonization is particularly rich in hydrogen, a fact which may become of considerable importance if hydrogenation processes develop. Already in the Claude synthetic ammonia process coke-oven gas is used as the source of hydrogen, the fractionation of the gas being done by liquefaction.

The applications of coke-oven gas in practice as a fuel evidently will be identical with those of coal gas, although the application in most cases clearly must be limited to certain special operations because of local conditions, so that the considerations relating to coal gas in the next section apply equally to coke-oven gas. It is, of course, essential that the latter shall be freed from tar and sulphur in the same manner as coal gas to conform with recognized standards.

COAL GAS FOR POWER PURPOSES

As the whole question of fuel consumption must be deferred until all the various fuels have been considered, it is only necessary to point out here that coal gas offers many advantages in the absence of space for fuel storage, space for boilers or producers, no stand-by charges, and constancy of supply, both in quantity and quality. The efficiency of the gas engine has increased to 37 per cent. and at or near full load gives frequently 30 per cent. effective output. Further, the efficiency from engines of moderate size to those of larger sizes is practically the same; it is only with smaller sizes that any marked difference is found.

Actual consumption in engines of moderate size frequently lies between 15 and 17 cu. ft. per B.H.P. hour, this being about 28 per cent. efficiency with gas of 570 B.Th.U. per cu. ft. net.

COAL GAS FOR INDUSTRIAL HEATING

Very great advances have been made in the application of coal gas for industrial purposes; advances in the construction of the burners and furnaces and in the application of high-pressure gas.

The advantages of coal gas as a fuel can be summarized as follows:

1. Gasification can be done at one point and clean gas distributed over a wide area.

2. No factory space is required for generators or storages.

3. Combustion and temperature control is simplified by the uniformity of the composition of the gas. The nature of the furnace atmosphere, whether oxidizing or reducing, can be easily adjusted.

4. The smoke and ash associated with solid fuels is eliminated and the gas contains no constituents which might injure the materials under treatment.

5. Greater economy is possible in furnace linings, melting-pots, crucibles, etc.

THE COMBUSTION OF COAL GAS AND GASEOUS FUELS

Three systems are available for the combustion of coal gas, in all of which the gas is burned as a non-luminous flame by the introduction of a proportion of air. In the first the gas and air are consumed at mains and at atmospheric pressure. In the second the gas is at mains pressure and the air at a higher pressure, and in the third the gas is at high pressure and the air at atmospheric pressure.

The first involves the use of burners of the ordinary Bunsen or atmospheric type, which are so well known that description is unnecessary. The general principle of their action is that the gas at main pressure, issuing through a jet, draws in sufficient air through suitable orifices to render the flame non-luminous. This is the *primary* air; it is insufficient for complete combustion, and the flame requires further air from the free atmosphere around for completing the combustion. This is the *secondary* air. The greater the ratio of the primary air to that theoretically required (about 5·5 times the volume of the gas) the smaller the flame and the more intense the combustion; hence the increased intensity of the blow-pipe flame.

H. Schmidt, by the optical pyrometer, estimated the highest temperature of the atmospheric gas flame to be 1800° C. (3720° F.), this occurring at the outer edge. Mahler estimated the average temperature of the coal gas flame as 1950° C. (3543° F.). Experiments by one of the authors with thermo-junctions of various diameters, so that exterpolation may be made for a couple of infinitely small diameter (i.e. radiation effect eliminated) obtained the following maxima, always in the extreme outer envelope, a short distance above the top of the burner:

	½″ Bunsen burner.		Kern burner.		
Gas per hour, cu. ft.	6·5	6·6	4·3	4·3	4·5
Ratio of primary air to gas	3·8/1	4·3/1	3·4/1	4/1	5/1
Maximum temperature, °C.	1720	1770	1610	1730	1860

Many successful furnaces of smaller size, working with gas at main pressure in free air, give excellent results, but are not so satisfactory as the other systems when accurate control of temperature is required.

The use of gas under high pressure generally has been more favoured than that of using air under pressure. It has been claimed that the variation in temperature is less with the former system and adjustment is more easy. There is no doubt but that accurate adjustment is possible with pressure gas, but with high-class pressure air burners, where mixing is very perfect, excellent results also are obtained. Further, rotary compressors are quite capable of giving the requisite pressure to air, but for higher pressures are mechanically inefficient.

Gas Burners. For the proper adjustment and mixing of the gas with the air required for combustion it is necessary to employ burners of different types to suit different conditions.

Domestic burners are chiefly of the Bunsen type in which the gas pressure is used to inject part of the air necessary.

The mixture of gas and primary air burns in an envelope of secondary air. The burner is designed to make the most efficient use of the gas pressure, the gas passing through an orifice or nozzle at as high a velocity as possible. Haslam gives the velocity of the gas as

$$\text{(I)}\quad V = 40{\cdot}4\sqrt{\frac{H}{D}} \text{ or } 59\sqrt{\frac{H}{D}}$$

for sharp-edged and tubular orifices respectively, where V = velocity in ft. per sec., H = gas pressure at orifice in inches of water, and D = gas density (air = 1) and the coefficients of contraction being 0·61 and 0·89.

As much air as possible is drawn in with the gas, the limiting factor being the amount of air which will cause the flame to strike back from the end of the burner tube to the jet. The tube carrying the mixture of gas and primary air, and the ports of the burner itself, should be such as to offer the minimum resistance to the flow of gases. Also the former should be so arranged as to avoid turbulence. The burner orifice may be either sharp-edged or tubular, the former ensuring a higher gas velocity for the same gas volume and therefore a greater efficiency of air injection.

Generally speaking, the greater the amount of primary air injected, the shorter the flame produced, or in other words, the greater is the rate of combustion. When the degree of aeration approaches 100 per cent. the height of the inner cone is small and is independent of air-gas velocity.

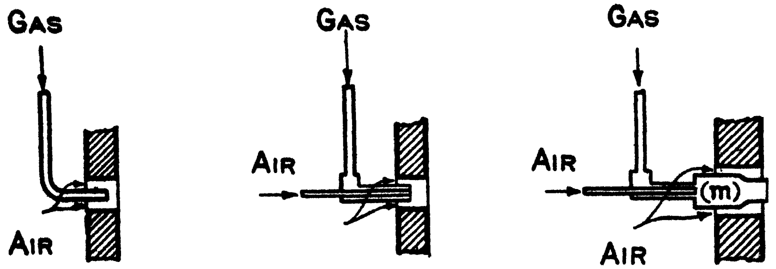
Burners used for industrial purposes are the same in principle, those used for rich gas employing primary air to make the combustion smokeless. The extent of mixing the gas and primary air controls the rate of combustion as before : (i) intimate mixing for development of a high temperature in a confined space, and (ii) delayed mixing where large spaces or surfaces must be heated without the development of too high or too local temperatures. Industrial burners may be of several types. The simplest takes the form of a combustion chamber into which gas and air, normally preheated, are led by separate streams. Other systems involve the separate introduction of primary and secondary air by induction or under pressure or both, or the intimate mixing of gas and air and the use of a high-velocity blast.

Figure 44 illustrates certain of the common types of burner used for different industrial purposes.

Types (*a*) and (*b*) are used where the gas is burned in combustion flues. Type (*c*) may also be used in this way, but high temperatures can be developed in restricted spaces. Type (*c*), where the gas and air are led in separately without any attempt at mixing can be used only for heating large spaces or extended flues. This type of burner has innumerable forms, in the simplest of which the air and gas enter the combustion chamber at a series of ports, the distribution of the gases being controlled by dampers over the ports. Type (*d*) is used where the gas is at a low pressure and injection in the form of a definite flame is desired.

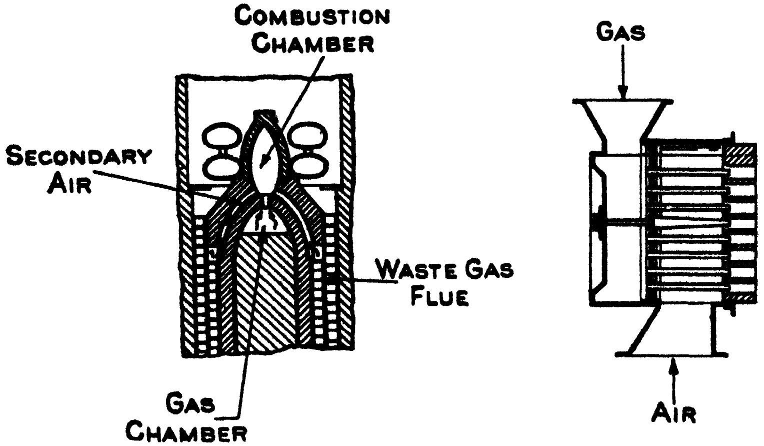
In heating large surfaces it is frequently necessary to liberate the heat from the gas in stages along heating flues. This can be done either by burning a limited quantity of gas with an excess of air at the point of introduction and introducing additional gas, without air, at suitable points, or by introducing all the gas with a limited primary air and completing the combustion by introducing secondary air at the necessary positions. A burner of the latter type is shown in Figure 45, designed at the Fuel Research Station for use with any type of fuel gas.

The gas enters a T-piece of large diameter, and the air supply, of



(*a*) Simplest Form with Induced Air Supply.

(*b*) Forced Primary Air and Induced Secondary Air or with Mixing Chamber (*m*).



(*c*) Separate Air and Gas Ports to Combustion Chamber, Low-grade Gas delaying Mixing for Heating Large Spaces.

(*d*) Producer Gas Burner using Compressed Air.

FIG. 44.—Types of Industrial Gas Burner.

smaller volume, enters via a nozzle into the gas stream. With such an arrangement the air can be varied within wide limits without making the flame smoky. In addition the CO_2 formed will prevent the formation of smoke when air is introduced at later points to complete the combustion. This burner operates equally well on water gas, producer gas or coal gas. With the latter the important dimension is the distance which the air nozzle projects beyond the centre line of the air supply.

If the amount of projection is too great the flame becomes smoky; if it is too little, or is negative, the burner becomes too hot or the flame backfires. In the case of the burner shown in Figure 45, the optimum conditions for smokeless combustion with rich gases are shown below:

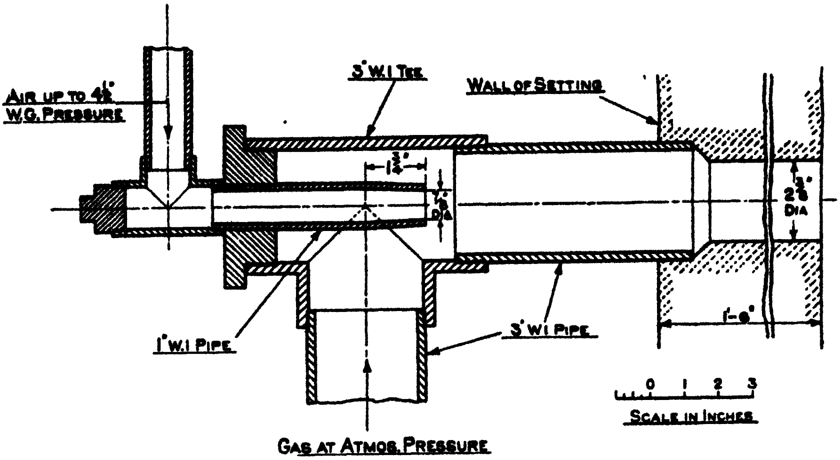


FIG. 45.—Fuel Research Gas Burner.

Gas.		Air volume—cu. ft.		Smoky.	Optimum Conditions.
B.Th.U.	Cu. ft. per hr.	Firing back.	Just luminous.		
587	510	1680 ratio 3·30	1150 2·25	832 1·63	1480 2·90
617	570	2030 ratio 3·57	1540 2·67	850 1·50	1790 3·14

In both cases smokeless combustion is achieved between fairly wide limits of gas/air ratio. In the above example the ranges are from 73 to 50 and from 74 to 56 per cent. of the theoretical amounts of air required for complete combustion of the gas. As the gas becomes richer, therefore, the range over which smokeless combustion is possible decreases, mainly because the lower limit at which luminosity appears rises.

S. N. Brayshaw (*Trans. Manchester Assoc. of Engrs.*, 1932–3 (7)) describes the method of operation which is adopted in the firing of small annealing furnaces with gas. The furnace is shown in diagram in Figure 46.

The gas and air enter as shown; the latter being heated in the recuperator R. This is of a spiral type to increase the rate and length of travel of the gas. Since perfect control of gas and air is necessary in a furnace of this type a proportioning valve can be used in which the gas and air ports open in unison by means of a pinion engaging upon segments which operate the valves. For a given gas movement of the pinion always gives the correct fuel mixture. In a furnace of this type 2 ft. wide × 1 ft. high × 3 ft. deep, 83 cu. ft. of gas of 452 B.Th.U. will maintain a temperature of 920° C.; the efficiency of the air preheater being over 40 per cent.

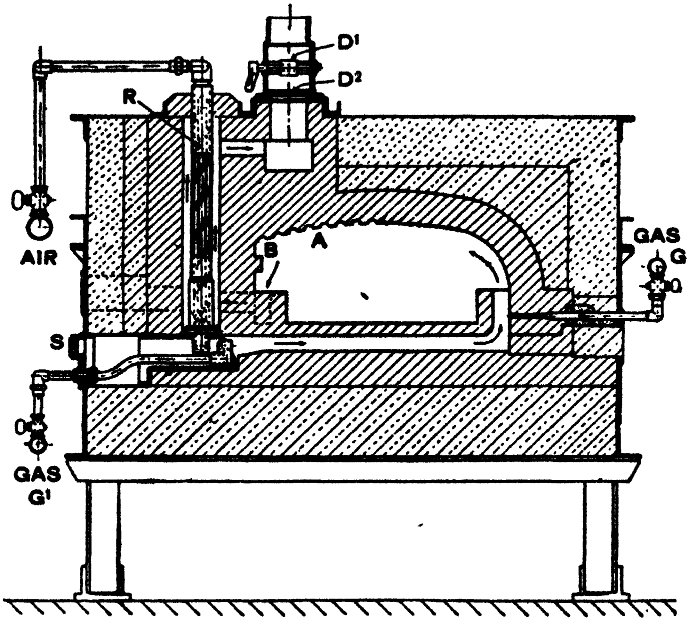


FIG. 46.—Brayshaw Annealing Furnace.

Surface Combustion. The development of means for increasing the rate of combustion of gas at a desired point is founded on the work of Bone, Wilson and McCourt, who followed up the original discovery of Davy that surfaces have the power of accelerating to a varying degree the rate of combustion of gas and air. At low temperatures only certain substances (e.g. platinum) have the property to a marked degree, but at high temperatures all substances are more or less alike.

Industrially the phenomenon is applied by the burning of the gas and air without flame at an incandescent surface, thereby ensuring perfect combustion at great rapidity, local application, high temperatures, and enhanced transfer of heat by increase in the rate of radiation.

The simplest form of apparatus in illustration of this principle is that where a flat diaphragm of porous but highly refractory material is provided with a shallow chamber at the back, to which a mixture of coal gas with slightly more than the theoretical amount of air is forced under pressure. Combustion takes place on the surface exposed to the air with such intensity that the refractory material is raised to a white heat. No flame whatever is visible, and that the air already mixed with the gas is sufficient for complete combustion is proved by immersing such a hot diaphragm in carbon dioxide, when no diminution of the action is noted.

The system is applied to crucible and muffle furnace heating by surrounding the crucible or muffle with granulated refractory material (generally carborundum), and forcing in the gas/air mixture at sufficient pressure to give velocity great enough to prevent back-firing in the explosive mixture. The difficulty has been to find materials sufficiently refractory to withstand the high temperatures. Platinum and alundum (nearly pure alumina) have been melted, and it is possible to maintain easily a constant temperature of 1500° C. (2732° F.).

The system has been applied to steam-raising and with the Bone-McCourt experimental boiler an over-all efficiency of 90 per cent. has been attained.

In its application for this purpose the boiler tubes were filled with broken refactory material to form the incandescent surface.

CHAPTER XIV

GASEOUS FUELS OF LOW CALORIFIC VALUE

Introduction. The underlying principle in the production of these gaseous fuels from solid fuels rich in carbon is the conversion of the carbon mainly into carbon monoxide, either by the action of air alone, steam alone, in which case approximately equal volumes of carbon monoxide and hydrogen are obtained, or by a mixture of air and steam. Obviously, the amount of heat available from a given weight of the solid fuel is unaffected whether the fuel is burnt directly on a grate, or is utilized indirectly by first gasifying and then burning the gases. The great advantages gaseous fuel undoubtedly offers in most cases can arise only from the better use, i.e. better efficiency, which can be made of the heat units of the fuel as a whole. Gaseous fuel can be more economical only when the higher efficiency attained in the combustion of the gas more than counterbalances the inevitable losses in the producer gas-cleaning plant, etc.

In comparison with solid fuel for furnace and general heating purposes the better results with the gaseous fuel depend on several factors. Although the theoretical amount of air for combustion is the same whether solid fuel is burnt directly on a grate to carbon dioxide, or burnt partially in the producer to carbon monoxide, the combustion of this gas being completed finally in the furnace, practically a considerable excess of air over that demanded by theory is requisite for fuel burnt on a grate, whilst, all told, as gaseous fuel the amount need barely exceed the theoretical. Where high intensity is required the excess air with solid fuel is often so large that the efficiency suffers. All excess air means great heat losses in the flue gases; losses mounting rapidly as higher temperatures of the flue gases are reached. The loss of sensible heat with gaseous fuel burning with a bare excess of air, even without any recovery, obviously will be less.

Further, much of this heat may be recovered in the latter case by the regenerative system of firing commonly employed. It is not a very practicable proposition to work on the regenerative system with solid fuel. The combination of the use of gaseous fuel with the regenerative system of firing alone permits of sufficiently high and regular temperatures for many metallurgical operations, as, for example, the production of open-hearth steel.

However carefully controlled the air supply may be with solid fuel, there is always some loss from incomplete combustion; with bituminous coal the loss of heat units through tarry vapours, etc., in the smoke is inevitable; with gaseous fuel used direct (without cooling, scrubbing, etc.), these heat units are rendered available; and absence of smoke is an important factor.

Again, better control of the temperature is possible, because of the ease of adjustment of the quantity consumed; more uniform heating effect over a large surface is attained, and at the conclusion of an operation the fuel supply can be shut off immediately. There is no fire to burn out.

Turning to power production, the saving in fuel by the direct use of these poorer gaseous fuels was formerly considerable, especially in comparison with steam. Advances in the use of steam, however, by the employment of high pressures and high superheats and the improvement of condensing plant and reheaters have now raised the thermal efficiency of the best steam-power plants to over 27 per cent. Although gas-power plants have also improved in efficiency so that 35 per cent. can be attained, higher maintenance costs have thrown the balance in favour of steam. Similarly, high maintenance costs have operated against the utilization of the still higher thermal efficiency of the Diesel engine in large power stations; variable fuel costs have also been a contributory cause. Power production from low-grade gaseous fuels has therefore become limited to smaller plants where some special cause such as isolation has been the deciding factor. The largest type of modern producer is now used mainly for furnace heating.

It is to be noted that the former belief that low-grade or dirty coals could be utilized to advantage in producers is dying out and that the modern producer calls for selected and closely graded fuel if high efficiency is to be maintained. Attention to this point makes small producer units still very efficient in comparison with steam, while in addition ease of distribution from a central plant is obvious.

Nature of Poor Gaseous Fuels. The fuels used for heating and power purposes are principally Producer gas and " Mixed " gas. Water gas is used to some extent for special heating operations, but is employed mainly as an addition to ordinary coal gas after the addition of hydrocarbon gases, having their source in higher petroleum oil distillates.

The action of air alone on carbon under producer conditions will give rise principally to carbon monoxide, diluted with the nitrogen originally present with the oxygen in the air. This is true of a fuel such as coke, which is free from bituminous matter. With a bituminous coal, the ordinary products of destructive distillation of the coal, i.e. coal gas, tar vapours, etc., will be present also; one ton of coal, for example, will yield some 11,000 cu. ft. of coal gas and about 112 lb. of tar; the gas and tar vapour therefore will add appreciably to the calorific value of the gas produced, which now contains methane, hydrogen, traces of illuminating hydrocarbons, etc.

The action of steam alone, as in one phase of operating a water gas plant, will give rise to about equal volumes of carbon monoxide and hydrogen, non-bituminous fuel chiefly being employed. The only diluting gases present should be those producer gases of the general composition given above which are left in portions of the plant.

In most cases of producer practice both air and steam are employed in the conversion of the solid into the gaseous fuel. The gases, therefore, partake of the component products of each reaction, the ratio of true producer gas to water gas depending primarily on the ratio of air to steam employed. This factor also exercises other important influences on the composition of the gas produced, as is discussed later. These gases are variously termed "producer" gas, which does not differentiate them sufficiently from a simple air-carbon gas; "Dowson" gas, after one of the pioneers; and "mixed" gas, which indicates more clearly that they are the result of the joint action of air and steam, and will be employed therefore throughout the subsequent pages. "Semi-water" gas is also employed frequently, and serves to indicate the joint reaction.

It will be clear that, except in the case of water gas itself, each of these producer gases must carry a large volume of inert non-combustible gas, the residual nitrogen from the air. The volume of true combustible gas present in relation to non-combustible is therefore low, and to this fact the low calorific value is due. The average composition, calorific value, and other data relating to gaseous fuels are shown in Table III, Appendix.

Where producer gases have to be employed in large heating furnaces the presence of suspended tar vapour derived from bituminous fuel is advantageous, because of the increased calorific value. Where such gases have to be supplied through cocks to burners or used in engines, the presence of suspended tar is inadmissible. The tar has to be sacrificed, and ample provision of cleaning plant provided for the gas. Sensible heat in the gases must at the same time be lost through the necessity of cooling and washing the gas. In some plants, however, attempts are made to convert the tar into permanent gases. Owing to the expense of erecting and operating devices for tar removal smaller-sized plants more usually are designed to work with non-bituminous fuels such as coke.

THEORY OF PRODUCER GAS REACTIONS

The primary reactions which have to be considered are those resulting from the action of an air blast and steam blast respectively on highly heated carbon. Although bituminous fuels are employed largely, these are still the principal gas-forming reactions, the only difference being that instead of the resulting gas being produced wholly by the air-carbon and steam-carbon reactions, it is composed in part of the destructive distillation gases, accompanied by tarry vapours, etc., which have to be removed. The gas is in fact a mixture of producer gas and coal gas, where bituminous coal is used, and consequently of higher calorific value.

Air-carbon Reaction. In ordinary processes of combustion of solid fuel, owing to the comparatively shallow layer of incandescent carbon and a relatively high air velocity, carbon dioxide is formed, and the greatest number of available heat units obtainable from the combustion of the fuel is arrived at. The reaction is

(*a*)

$$\underset{12\text{ lb.}}{C} + \overbrace{\underset{32\text{ lb.}}{O_2} + (\text{nitrogen})}^{\text{Air}} = \overbrace{\underset{44\text{ lb.}}{CO_2} + (\text{nitrogen})}^{\text{Flue Gases}} + 174{,}060 \text{ B.Th.U.}$$

As is well known, too great a depth of fuel may give rise to the formation of carbon monoxide, with corresponding loss of available heat units. With sufficient depth of highly heated carbon in relation to the air velocity, carbon monoxide alone may be the final product, or at least with only certain traces of carbon dioxide, the reaction being:

(*b*)

$$\underset{24\text{ lb.}}{2C} + \overbrace{\underset{32\text{ lb.}}{O_2} + (\text{nitrogen})}^{\text{Air}} = \overbrace{\underset{56\text{ lb.}}{2CO} + (\text{nitrogen})}^{\text{Producer Gas}} + 103{,}530 \text{ B.Th.U.}$$

Most recent researches show that the action of oxygen on carbon results in the simultaneous formation of carbon dioxide and carbon monoxide, but with a sufficient depth of fuel any carbon dioxide reacts with more carbon, producing carbon monoxide, so that for all practical purposes the above equation represents the net result in a producer.

The thermal efficiency as a gas-making machine will be given by $\frac{14{,}505 - 4350}{14{,}505} \times 100 = 70$ per cent. approximately. This is the efficiency with no sensible heat units in the gases produced, and is termed the *cold* gas efficiency. In practice the gases leave the producer at a very high temperature, often 800–900° C. (1470–1650° F.), so that the *hot* gas efficiency equals the cold gas efficiency plus the sensible heat of the gases. This may be equal to 85 or even 90 per cent.

The above reaction is *exothermic*, and the temperature in a producer blown with air will continue to rise for a given air blast until counterbalanced by losses of sensible heat in the gases, in the ashes and clinker, by radiation, etc. A limit is soon reached in practice beyond which it is undesirable to go, this being determined in general by the liability to form clinker from the ash of the fuel and trouble with the producer linings. The controlling medium employed almost universally to regulate the temperature is steam.

Steam-carbon Reaction. When steam is blown through a bed of incandescent carbon the following reactions may occur.

(*c*) $C + H_2O$ (steam) $\longrightarrow CO + H_2$ $-$ 52,200 B.Th.U. at 15° C.
12 lb. + 18 lb.

(*d*) $C + 2H_2O$ (steam) $\longrightarrow CO_2 + 2H_2$ $-$ 34,000 B.Th.U.
12 lb. + 36 lb.

(*e*) $CO + H_2O$ (steam) $\longrightarrow CO_2 + H_2$ $+$ 16,400 B.Th.U.
28 lb. + 18 lb.

(*f*) $C + CO_2 \longrightarrow 2CO$ $-$ 70,200 B.Th.U.
12 lb. + 44 lb.

(*g*) H_2O (water) $\longrightarrow H_2O$ (steam) $-$ 19,040 B.Th.U.
18 lb.

Clement, Adams and Haskins (U.S. Bureau of Mines, Bull. No. 7, 1911) have shown that, normally, reaction (*c*) predominates, (*d*) is relatively small and that (*e*) and (*f*) operate as shown, to the right. Reaction (*c*) requires a relatively high temperature, over 900° C. (1650° F.), whereas reaction (*d*) predominates at low temperatures (500° C. or 930° F.).

Reactions (*c*) and (*d*) are markedly *endothermic*, requiring respectively 4350 and 2830 B.Th.U. per lb. of carbon. It follows that if a producer be blown to a high temperature with air, either with the formation of carbon monoxide or a mixture of this gas and carbon dioxide, depending upon conditions referred to above, and then steam be substituted, the reaction (*c*) takes place at first, the temperature falls rapidly, and the reaction (*d*) asserts itself more and more. When the air and steam blasts are used independently, as is the case in water-gas practice, a point is soon reached when the production of carbon dioxide is so excessive (this gas being inadmissible in any quantity for the principal purpose for which water gas is employed) that steam must be cut off and the producer blown once more with air up to the proper temperature. The process is intermittent, consisting of alternate air "blows" and steam "runs."

Clearly, by the simultaneous action of air and steam it will be possible to make such a thermal balance between the air-carbon (exothermic) reaction and the steam-carbon (endothermic) reaction that a constant temperature, dependent on the relative proportion of air and steam may be maintained, and corresponding with this temperature a definite composition for the "mixed" gas obtained will be attained, depending on the relative parts played by the reactions (*b*), (*c*) and (*d*).

Steam then affords a practical means of controlling the producer temperature, of avoiding all those troubles associated with high temperatures, and, moreover, by producing a gas consisting almost wholly of two gases of high thermal value instead of simple producer gas with some 65 per cent. of inert gas (nitrogen), the resulting mixed gas is richer and of higher thermal value through its employment.

By making certain arbitrary assumptions, including that of thermal perfection, it is possible to calculate the composition, thermal value, etc., for the "mixed" gas theoretically obtained for any given air-steam ratio, but such results are inevitably far removed from those attained in practice, so that it is not proposed to introduce such calculations.

Reversible Reactions in Producer Practice. Further important considerations govern the composition of the resulting gases. In the air-carbon reaction, allowing that all the oxygen already has entered into some form of combination with carbon, there exists simultaneously in the producer hot carbon, carbon dioxide and carbon monoxide. Carbon can react with any carbon dioxide with the formation of carbon monoxide ; conversely, under some conditions the reaction may reverse, and carbon monoxide yield carbon and carbon dioxide. This is a *reversible reaction*, and is expressed as—

$$C + CO_2 \rightleftarrows 2CO$$

The reaction ⟶ is *endothermic* ; the reaction ⟵ is *exothermic*.

For a given temperature, in time an equilibrium between the two reactions in either direction will be set up. At high temperatures this equilibrium is attained far more rapidly than at low temperatures. Rhead and Wheeler (*J.C.S.*, 1910, 2178) showed that at 850° C. (1560° F.) equilibrium was attained in this mixture only in 240 hours, whilst at 1000° C. (1830° F.) or over it was attained in 48 hours. Further, they showed that at 850° C. the reaction $CO_2 + C = 2CO$ proceeded 166 times more rapidly than the reverse reaction.

In practice the formation of the maximum of carbon monoxide and minimum of carbon dioxide is what is aimed at. High temperatures clearly favour this ; pressure (i.e. concentration) on the right-hand side, where the volume of carbon monoxide is double that of the dioxide tends in the reverse direction, but, as shown, this is a very slow reaction, and moreover in practice, the carbon monoxide is being withdrawn continually from the system ; in other words, its removal accelerates the rate at which it is being produced.

In a valuable contribution on the "Essential Factors in the Formation of Producer Gas," Clements, Adams and Haskins (*loc. cit.*) give results for equilibrium established when carbon dioxide is passed through tubes containing carbon in various forms. Similar experiments were conducted with air and coke and the graphs which can be plotted from the results are most illuminating.

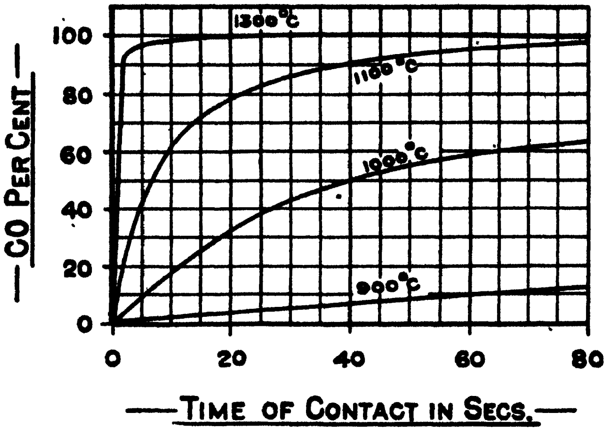


Fig. 47.—Effect of Temperature and Time of Contact on the Production of CO from Coke and CO_2.

Figure 47 shows the results obtained with carbon dioxide and Figure 48 those obtained with air. Figure 47 shows clearly the decrease of time of contact with temperature to obtain a gas of a given CO content. In considering Figure 48 it should be taken that the usual time of contact in a gas producer is about 1 second. A general conclusion is that the gas of highest CO content is obtained by increasing the time of contact and the reaction temperature to their practical limits.

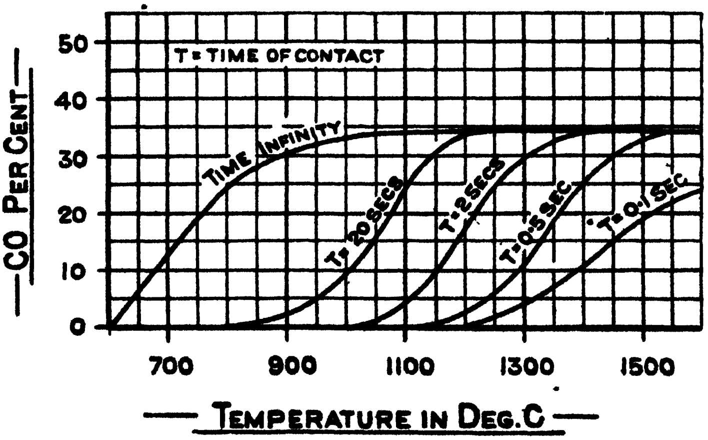


Fig. 48.—The Production of CO from Coke and Air at Different Temperatures.

The actual attainment of the equilibrium in a producer blown with air is well shown from results obtained by Wendt (*Stahl und Eisen*, 1906, 26, 1184); the fuel depth was 7 ft. 6 in.

TABLE XLIX

COMPOSITION OF GASES FROM PRODUCERS (Wendt)

Height above tuyère.	Temperature ° C.	Composition of the gas.				
		Carbon dioxide.	Carbon monoxide.	Hydrogen.	Methane.	Nitrogen.
At outlet .	580	0·7	31·3	6·3	2·4	59·3
60 in. . .	—	1·0	28·9	9·8	2·0	58·3
50 „ . .	1030	0·6	30·0	11·7	0·6	57·1
40 „ . .	—	0·4	33·4	2·4	0·3	63·5
30 „ . .	1250	*nil*	34·5	0·4	*nil*	65·1
20 „ . .	—	0·2	34·3	*nil*	*nil*	65·5
10 „ . .	1400	0·2	34·1	*nil*	*nil*	65·7
At tuyère .	—	15·0	9·7	*nil*	*nil*	75·3

Equilibrium was established somewhere between 20 and 30 in. above the tuyères. The reversal of the action as the gases passed to a zone at lower temperature is shown by the slight increase of carbon dioxide at higher levels. Methane and hydrogen result from the use of bituminous coal; they make their appearance in the upper part of the producer, being eliminated completely by destructive distillation before the air-carbon reaction is set up.

More important reversible reactions occur when steam is employed. In this case varying proportions of carbon monoxide, carbon dioxide, hydrogen and steam will be coexistent, and by their interaction at various temperatures a constant composition for a given temperature will tend to be obtained. The reactions may be expressed:

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

The reaction ⟶ is *exothermic*; the reaction ⟵ is *endothermic*.

The composition of the ultimate "mixed" gas clearly will be dependent largely on the relative rate at which change is progressing in either direction. For any given temperature this depends on the relative mass (or concentration) of the gases on either side; that is, a constant K for the ratio $\frac{CO + H_2O}{CO_2 + H_2}$ will result. This constant has been determined by Oscar Hahn as follows:

Temperatures ° C.	K	Temperatures ° C.	K
786	0·81	1086	1·95
886	1·19	1205	2·10
986	1·54	1405	2·49

In all ordinary practice, where a temperature of about 1000° C. (1830° F.) is usual, the constant is about 2. Should the gas be of other composition than that agreeing with this constant 2, and attain—either in the producer or regenerator—a temperature of about 1000° C., it will tend to undergo such of the reversible changes referred to as will bring its ultimate composition into agreement with this constant.

Lowering of temperature clearly will result in an increase of carbon dioxide at the expense of carbon monoxide. Again, rise of temperature will result in an increase in the amount of carbon monoxide present in the dry gas, with a corresponding decrease in the hydrogen and carbon dioxide. This is of great importance where the gas passes through regenerators, as is so frequently the case, and the issuing hot gases will be markedly different in composition from the original. A further point of note is that increased concentration of steam, apart from its effect in lowering the temperature and hence the value for K, by the increase of the concentration on the left-hand side of the equation will determine further a greater proportion of carbon dioxide and hydrogen in the gases.

Other experimental results by Wendt in a producer blown with air saturated with steam at 60° C. (140° F.) illustrate this change.

TABLE L

Composition of Producer Gases with Air-steam Blast (Wendt)

Height above tuyère.	Temperature° C.	Composition of the gas.					
		Carbon dioxide.	Carbon monoxide.	Hydrogen.	Methane.	Nitrogen.	Oxygen.
At outlet .	440	5·5	26·8	14·6	3·4	49·7	—
60 in. .	—	5·3	28·0	19·0	4·1	43·6	—
50 ,, .	810	6·0	28·3	20·7	4·8	40·2	—
40 ,, .	—	5·0	28·7	21·8	5·0	39·5	—
30 ,, .	925	3·0	32·7	17·9	1·2	45·2	—
20 ,, .	—	5·5	28·0	13·7	0·9	51·9	—
10 ,, .	—	9·3	22·0	10·8	0·4	57·7	—
At tuyère .	1110	11·4	*nil*	*nil*	*nil*	79·1	9·5

The increase of carbon dioxide and decrease of carbon monoxide above 30 in. is shown clearly. Towards the top of the producer the diluting effect of the distillation products of the coal masks the results somewhat. The hydrogen and methane both result partly from the bituminous constituents of the coal and partly from the action of the steam on carbon. In the United States tests referred to above it was noted that at high temperatures and low velocity about 2 per cent. of methane was found in the gases from the steam-carbon reaction.

The course of the reactions in a gas producer can be followed more closely by withdrawing gas samples from the fuel bed at different levels. As soon as the air passes the ash layer and reaches the fuel bed reaction begins. In the next 3 to 4 in. the oxygen is entirely consumed and the CO_2 content of the gases rises proportionately. After this initial rapid increase CO is formed by the reaction $CO_2 + C = 2CO$ and the amount of CO_2 decreases, at first rapidly. These two zones are respectively the oxidation and reduction zones of the producer.

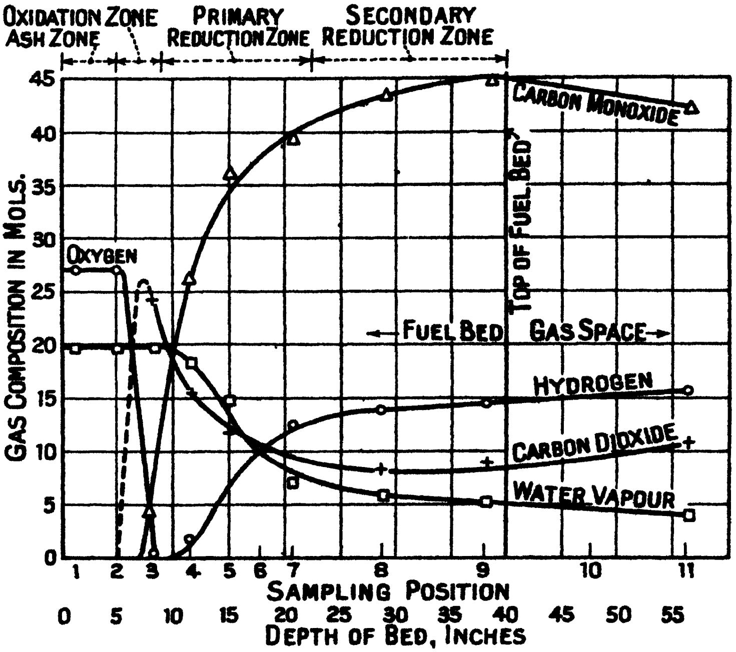


FIG. 49.—Composition of Gases in the Fuel Bed of a Gas Producer. Basis, 100 Mols. of N_2, Anthracite or Coke (Haslam, Entwistle and Gladding).

After a further 12 in. the CO and CO_2 reach an approximate state of equilibrium depending upon the distribution of temperature.

In the oxidation zone the water or steam remains unchanged and decomposition of H_2O does not begin until the formation of CO has started. The formation of hydrogen increases rapidly over a distance of about 12 in. and then decreases slowly owing to the falling temperature of the bed.

Experiments on these lines by Haslam, Entwistle and Gladding (*Ind. Eng. Chem.*, 1925, **17**, 586) have provided sufficient data to express the results graphically.

In Figure 49 the proportions of the different gases produced are shown graphically in terms of molecules of each constituent per 100 molecules of nitrogen, this gas remaining unchanged in the process. The volumes of the gas are, of course, in the same proportions. Starting with air containing 79 per cent. of nitrogen the volume of oxygen corresponding to 100 mols. of nitrogen is 26·6 mols. It is shown that this oxygen is distributed between the CO and CO_2 produced in the proportions of 22·6 to 4·0.

The reactions taking place, and their zones, are shown diagrammatically in Figure 50. In the *oxidation zone* there is only one reaction

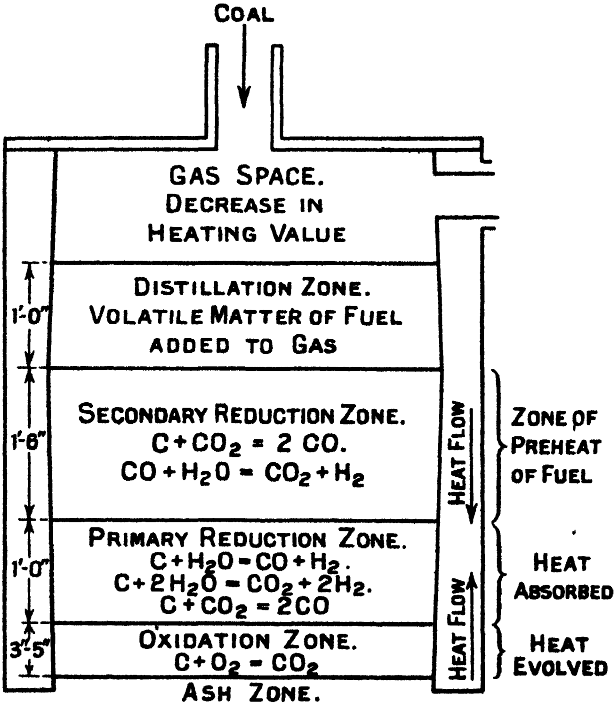


FIG. 50.—Reactions in a Gas Producer.

as shown and, owing to its strongly exothermic character this is the hottest zone of the producer.

In the next zone three reactions occur in which the CO_2 and steam are reduced to CO and H_2 respectively, mainly by solid carbon. This is a narrow zone (about 14 in.) and is termed the *primary reduction zone* since the action is mainly that of the solid carbon. Above this zone further reduction of the CO_2 continues, but CO_2 is also formed by interaction between CO and steam. The extent of these reactions is comparatively slight. Since steam is not decomposed by carbon in this zone it is termed the *secondary reduction zone*. The main function of the zone is to act as a heat exchanger in which the descending fuel is heated by the rising hot gases; a deep zone is therefore normally advantageous. In the final zone the fuel is also pre-heated and, in the case of coal, distilled, the volatile matter enriching the producer gas.

Above the fuel bed loss of calorific value can result if the temperature is too high owing to the reversal of the reaction $CO_2 + C \rightleftharpoons 2CO$ in the absence of carbon. Working with a deep fuel bed is one means of preventing this loss, which may be as high as 10–15 per cent.

Advantages through Introduction of Steam. The importance of steam in gas-producer practice is so great that it is desirable to summarize its advantages. These are chiefly:

1. Enables efficient control of the temperature to be maintained.

The higher the temperature the better the gas is, in general, an axiom, but the permissible maximum temperature varies with the class of fuel; principally with the liability of the ash to fuse and form clinker; to a less degree with the effect of high temperatures on the firebrick lining of the producer.

2. By the gasification of a considerable proportion of the carbon by steam instead of wholly by air the gas contains less inert nitrogen (derived from the air), since that portion gasified by steam yields almost wholly combustible gases (carbon monoxide and hydrogen) of high calorific value.
3. The lower temperature of the producer means a lower temperature of the issuing gas; less sensible heat is therefore carried by the gases, and since the proportion of combustible gases is higher, they carry a greater potential heat which is rendered available on combustion.

Sensible heat units in the hot gas are not nearly as efficient as the corresponding number of heat units available on combustion. In many cases where the gases are cooled before use, with loss of a part and frequently nearly the whole of the sensible heat units, the use of steam proves an economical method of rendering heat units available which otherwise would be lost. In other words, steam transfers heat from where it is not wanted beyond a certain degree to the furnace or engine where these units can be utilized profitably.

The effect of steam in gas-producer practice was first investigated fully by Bone and Wheeler (*Engineering*, 1907, **83**, 659; 1908, **86**, 837). Two series of experiments were conducted in a Mond plant with fuel beds of 7 ft. and 3 ft. 6 in. respectively. The principal data from these trials are given in Table LI. The calorific value of the gas and the thermal efficiency of the process were found to reach maxima when the steam used was from 0·45 to 0·50 lb. per lb. of fuel. At this rate 80 per cent. of the steam was decomposed.

TABLE LI.

STEAM IN GAS PRODUCER PRACTICE (Bone and Wheeler)

	Series 2 (3 ft. 6 in. bed).				Series 1 (7 ft. bed).				
Saturation temp. of blast. C. °	45°	50°	55°	60°	60°	65°	70°	75°	80°
Lb. of steam in blast per lb. coal gasified	0·2	0·21	0·325	0·454	0·45	0·55	0·80	1·10	1·55
Percentage of steam decomposed	100	95	100	76	87·4	80·0	61·4	52·0	40·0
Cu. ft. of air (at 0° C. and 760 mm.) in blast per lb. of dry coal gasified	38·8	38·6	36·75	37·45	36·95	34·9	36·8	36·9	37·1
Ratio of $\frac{\text{oxygen from steam}}{\text{oxygen from air}}$	0·33	0·30	0·42	0·44	0·50	0·62	0·65	0·75	0·80
Yield of gas in cu. ft. at 0° C. and 760 mm. per ton of dry coal	133,700	132,500	132,700	135,000	138,250	134,400	141,450	145,800	147,500
Composition of the gas. Carbon dioxide	2·35	2·50	4·40	5·10	5·25	6·95	9·15	11·65	13·25
Composition of the gas. Carbon monoxide	31·60	30·60	28·10	27·30	27·30	25·40	21·70	18·35	16·05
Composition of the gas. Hydrogen	11·60	12·35	15·45	15·50	16·60	18·30	19·65	21·80	22·65
Composition of the gas. Methane	3·05	3·00	3·00	3·05	3·35	3·40	3·40	3·35	3·50
Composition of the gas. Nitrogen	51·40	51·55	49·05	49·05	47·50	45·90	46·10	44·83	44·55
Composition of the gas. Total combustibles	46·20	45·95	46·60	45·85	47·25	47·10	44·75	43·50	42·20
Calorific value of the gas. B.Th.U. per cu. ft. gross	180·0	178·5	180·8	178·7	185·5	185·5	177·5	172·1	169·5
Calorific value of the gas. „ „ net	170·5	168·7	169·1	166·9	173·0	172·0	163·3	157·3	153·5
Efficiency ratio, including steam for blower	0·73	0·718	0·722	0·725	0·778	0·750	0·727	0·701	0·665

With a 7-ft. fuel bed the producer used consumed about 10 tons of dry coal per day.

The effect of much undecomposed steam in gases will be to lower greatly the efficiency. A quantity of steam will carry a large amount of sensible heat at the temperature of the escaping gases, in addition to the quantity of latent heat also present. It is the necessity of recovering this sensible and latent heat in the excess steam, which must be used when ammonia recovery is attempted, which accounts largely for the extra plant and cost entailed when ammonia recovery is required, and determines whether recovery will pay.

In Series 2 further reduction of the saturation temperature below the 60° C. (which was the lowest in Series 1) had little effect on the thermal efficiency and no marked effect on the yield of gas or its calorific value. There appears to be no gain in reducing the saturation temperature below this, and its reduction would lead probably to clinkering troubles. At 45° saturation the temperature was so high that the ash fused and ran through the bars. It is of interest to note, in view of the reversible changes already referred to and the possibility of such reversal occurring in regenerators, that the gas obtained at 55° saturation was in equilibrium for a temperature of 1100° C., and passed through regenerators at this temperature unchanged.

One of the most important comparisons possible from Bone and Wheeler's results is that between the results when the fuel depth was halved and the rate of gasification almost doubled, for the same saturation temperature (60° C.). The composition of the gas was but little altered; there was rather more combustible present with the deep bed, and consequently the gas had a slightly higher thermal value. The efficiency with the deep fuel bed was some 5 per cent. higher than with the shallow bed and higher rate of gasification. It is clear that the shallow bed of 3 ft. 6 in. was quite capable of giving satisfactory results, even with a rapid gas output, and since clinkering troubles are more likely to occur with greater fuel depth, clinker tending especially to grow on the firebrick sides of the producer, there is a distinct practical advantage in keeping the depth of the fuel as shallow as is consistent with the formation of good gas at a fairly rapid rate of working. A fuel with caking tendencies demands a greater depth than a non-caking fuel, owing to the liability of air channels forming.

The relative depth of the total-fuel content to that of the highly incandescent portion may have an appreciable effect, in view of these reversible changes, on the composition of the gas issuing finally from the producer, providing the time necessary for appreciable change is allowed. Above the high temperature zone will be a layer of constantly decreasing temperature, in which reversal with the production of carbon dioxide and hydrogen will tend to occur.

The effect of steam on gas coke has similarly been investigated by Gibson and Gwyther (*Trans. Instn. C.E.*, 1909, **177**, Part iii) using a small 30 H.P. suction-gas producer. The proportion of water added was varied by controlling the saturation temperature of the air between 86 and 147° F. The results are shown graphically in Figure 51. The following are the effects of increasing the steam added:

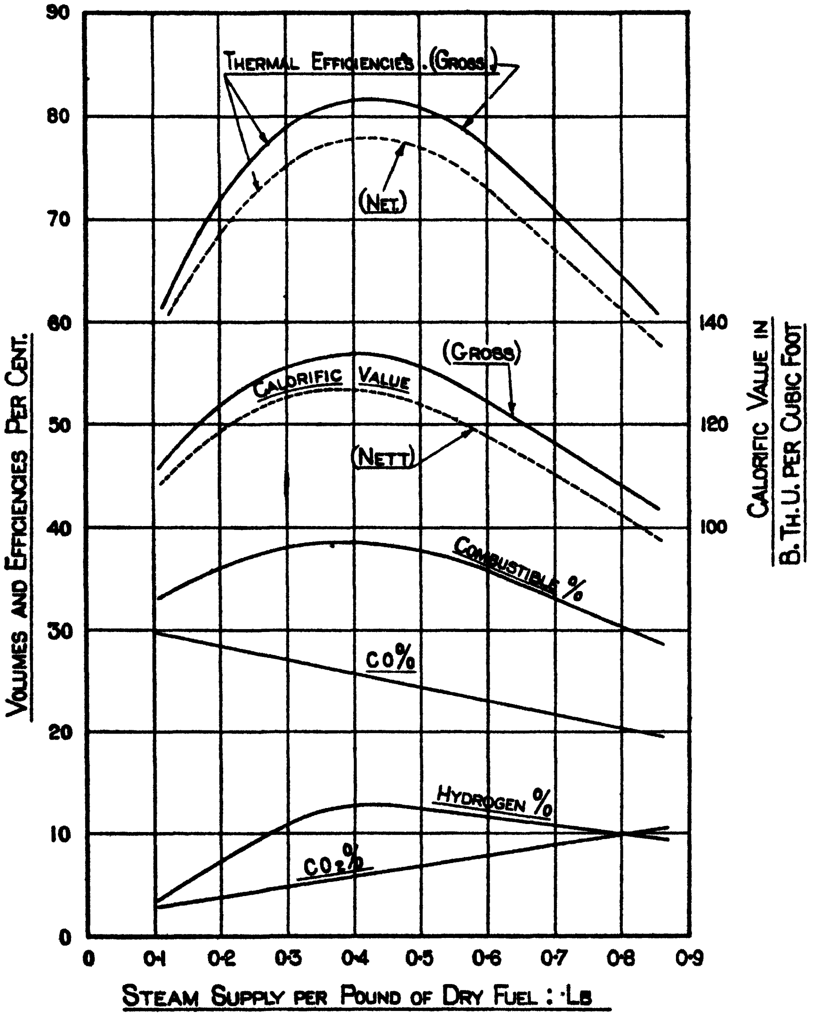


Fig. 51.—Effect of Steaming on Gas Producer Efficiency.

(i) The percentage of CO_2 in the gas increases steadily while that of CO decreases steadily.

(ii) The percentage of hydrogen increases to an optimum at 0·4 lb. water per lb. of fuel, and then decreases.

(iii) The calorific value and thermal efficiency curves show similar optimum points.

Up to the point of optimum hydrogen production the water vapour supplied is completely decomposed, the saturation temperature being 125° F. At higher saturation temperatures the percentage conversion gradually falls off, although the weight decomposed increases. The decrease is due to decrease of fuel temperature.

Under theoretical conditions of no loss of heat by radiation, etc., the optimum figure for steam would rise to 0·636 lb. per lb. of carbon gasified as against 0·5 in the above experiment. Similarly, the thermal efficiency would rise from the 78·6 per cent. shown to 95·2 per cent.

N. E. Rambush (*J. W. of Scot. Iron and Steel Inst.*, 1922–3) has discussed the effect of steam and time of contact with the fuel on the production of ammonia. He points out that the ammonia is derived from (*a*) simple distillation of the volatiles, (*b*) interaction of the residual nitrogen compounds with the gases. It is generally accepted that for the recovery of ammonia a large excess of steam is desirable ; it lowers the temperature of the producer, and, together with dilution of the escaping gases by undecomposed steam, prevents decomposition of ammonia when formed. Rambush claims equally good results with much less steam than is customary by allowing a much longer time of contact in the producer, whereby interaction between the residual nitrogen compounds and the steam or hydrogen increases the actual production of ammonia, and, further, by suitable increase in the depth of fuel a low exit gas temperature is produced. The following results confirm these views, figures from Bone and Wheeler's results, Series I, 80° saturation, being included for comparison :

	Saturation temperature °C.	Time factor seconds.	Lb. of steam per lb. of fixed carbon gasified.		Percentage of nitrogen in coal obtained as ammonia.
			Added.	Decomposed.	
I.	80	1·7	2·64	1·06	49·0
II.	85	1·45	4·24	1·27	61·5
III.	78	3·5	2·55	1·58	60·0
IV.	75	>5·0	1·75	1·58	57·5

I. Bone and Wheeler, Series I.
II. Mond plant.
III and IV. "Low temperature" producer.

The question of ammonia recovery is now of little importance owing to the rise of the synthetic ammonia industry.

CHAPTER XV

WATER GAS AND TOTAL GASIFICATION

WATER GAS

Water gas is produced by the action of steam on carbon at a high temperature, to ensure the reaction taking, as completely as possible, the form :

$$\underset{12\text{ lb.}}{C} + \underset{18\text{ lb.}}{H_2O}\text{ (water)} = CO + H_2 - 71{,}240\text{ B.Th.U.}$$

Theoretically, then, water gas consists wholly of two combustible gases of practically the same gross calorific value per cubic foot. In actual practice a small quantity of carbon dioxide results from the reaction :

$$\underset{12\text{ lb.}}{C} + \underset{36\text{ lb.}}{2H_2O}\text{ (water)} = CO_2 + H_2 - 72{,}080\text{ B.Th.U.}$$

According to the theory already given, the proportion of gases formed by this latter reaction increases with lower temperatures of operating. In addition to the non-combustible gas, carbon dioxide, small quantities of nitrogen, and occasionally a little oxygen accompany the gas, these being residual gases in certain portions of the apparatus from the air blast which precedes the steam blast. The following range of composition is deduced from a number of analyses :

Hydrogen	45–51	per cent.
Carbon monoxide	40–45	,,
Carbon dioxide	3–6	,,
Nitrogen	3–7	,,
Methane	0·1–0·5	,,

The calorific value of water gas is about 300–310 B.Th.U. gross, and 280–290 B.Th.U. net per cu. ft. The calorific intensity of the water-gas flame is high.

Since water gas contains only traces of methane and no unsaturated hydrocarbons, it burns with a bluish non-luminous flame. For its principal application—as an addition to coal gas—water gas is "carburetted" to render it luminous ; the uncarburetted gas is sometimes known as "blue" water gas.

Carburation of the gas may be attained by either a hot or cold process. In the former, suitable oils are "cracked" by subjection to a high temperature, the resulting oil-gas, of high illuminating power, mixing with the non-luminous water gas; in the latter, volatile tar spirits are vaporized to confer the necessary illuminating power (benzole enrichment).

The manufacture of carburetted water gas is now a most important operation in the coal-gas industry; the annual production in 1931 and 1933 has already been given (p. 260). The consumptions of coke and oil approximate to 44·0 lb. and 1·30 gals. per 1000 cu. ft. of gas produced.

Before the conditions of use of coal gas changed so that it is no longer a necessity that its illuminating power shall be high, the gas resulting from high-temperature distillation of ordinary coal in small charges seldom reached the necessary standard of illuminating power. Prior to 1889, a proportion of cannel coal was generally retorted to raise the illuminating power, and the high price of cannel rendered this system of enrichment expensive. By the use of carburetted water gas enrichment is obtained at a much lower cost, and other economical advantages have contributed greatly to the extension of its use; among these may be mentioned that a water-gas plant enables the gasworks manager quickly to meet a rapid demand for gas owing to fogs, etc.; it provides a use for a considerable proportion of the coke produced in the gas retorts, so helping to maintain a fair price for the surplus available for outside disposal; it enables a smaller stock of coal to be maintained; and, lastly, leads to economy in labour, so that although its use specifically to give added illuminating power does not hold so generally as in the past, its other advantages may determine the continuation and extension of its use in gasworks' practice.

The composition of carburetted water gas is:

Authority:	Körting.	Spiers.
Hydrogen	34–38	37·0
Carbon monoxide	23–28	30·5
Saturated hydrocarbons	17–21	14·0
Unsaturated hydrocarbons	13–16	7·4
Carbon dioxide	0·2–2·2	5·6
Nitrogen	2·5–5·0	5·5

The theoretical considerations governing the production of water gas have been given already. One point only demands further reference. It has been shown (Equation *c*, p. 276) that in the decomposition of 1·5 lb. of steam by 1 lb. of carbon, in the ideal water-gas equation, 4350 B.Th.U. must be supplied. Many attempts were made to obtain this heat by the combustion of carbon in a furnace built around the generator in which the actual production of water gas was being carried on; the process would then be a continuous one, but all such attempts have resulted in failure in practice.

Recourse therefore must be made to an intermittent method, in which the fuel first is heated to high incandescence by an air blast, and then the steam passed through the same generator until the temperature has been reduced below the point at which good gas can be obtained. The process thus demands alternate " blows " with air, and gas-making periods, " runs," where steam is employed.

Any intermittent process necessarily suffers from certain disadvantages as compared with a continuous one. Either a gasholder must be provided in which to collect the water gas, or more than one producer must be installed, the number depending on the relative duration of the " blow " and " run " periods. Further, owing to the endothermic character of the steam-carbon reaction, the producer is working at a constantly falling temperature during the run; the gas consequently is not of constant composition, and, as shown by theoretical considerations already given, the carbon dioxide present will increase steadily in amount.

According to Equation *b* (p. 275), if the air blast results simply in the production of carbon monoxide, 4314 B.Th.U. are available per lb. of carbon gasified. It follows that per lb. of carbon converted into water gas $\frac{4350}{4314}$, or a little more than an equal weight of carbon must be used for the air-carbon reaction. On the other hand, if the working conditions could be made such that carbon dioxide alone resulted in the air blast, giving according to Equation *a* (p. 275) 14,500 B.Th.U., then the carbon for supplying the heat for 1 lb. of carbon converted to water gas would be only $\frac{4350}{14,500} = 0{\cdot}30$ lb.

The process of Lowe and Tessié du Motay originated in America in 1873, but the blow period was used to make producer gas containing 30 per cent. of carbon monoxide. Since the idea of the blow is to store as much heat in the generator as possible with the expenditure of as little coke as possible, blowing to CO_2 only would be advantageous. This was suggested by Dellwik, who advocated shallow fuel beds with which the CO_2 content of the blow could be raised to 18–20 per cent. Modern practice is something of a compromise, the blow gases containing from 12–14 per cent. of CO_2 and 12·5 to 10·5 per cent. of CO. Under these conditions the carbon consumed during the blow is approximately equal to that consumed in making the water gas.

Manufacture of Water-Gas. It is best to consider the manufacture of " blue " water gas before dealing with the more complicated systems for " carburetted " water gas. Water gas is normally made from fuels such as coke or anthracite which contain very little volatile matter. The range of composition of the gas has been given above. Apart from these constituents water gas contains H_2S (about 80 grains per 100 cu. ft.) and traces of iron carbonyl. It generally contains as a solid impurity fine dust consisting mainly of silica and sulphur, which causes difficulty owing to deposition in pipes and at burners. Owing to its high production cost in comparison with producer gas, blue water-gas plants are not common, the gas being made mainly for certain industrial applications, e.g. where a high flame intensity is required. Recently a demand for large plants has arisen in connection with the synthetic ammonia and synthetic fuel oil industries; the generators compare in size with those used in the manufacture of carburetted water gas.

In its simplest form a water-gas generator, Figure 52, is a brick-lined steel casing containing the fuel bed, supported on a suitable grate, and with air, steam and fuel supplies and a stack for the escape of blow gases.

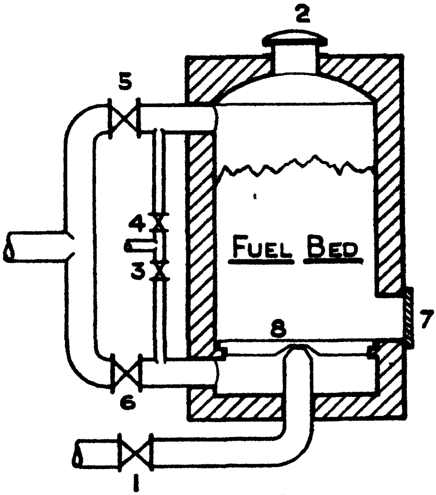


FIG. 52.—Diagrammatic Section of Water-gas Generator.

The valves are arranged for central control and the plant is operated on a time cycle as follows, assuming the fuel bed to be approximately at the working temperature:

1. Blow with air (1) with stack valve (2) open for say 60 seconds.
2. Open lower steam valve (3), wait a few seconds for water gas to clear the blow gas through the stack valve. Close stack valve and open gas valve (5) to scrubber.
3. Steam for say one minute.
4. Close lower steam supply (3) and open upper steam supply (4). Close upper gas valve (5) and open lower gas valve (6).
5. Steam for say two minutes downwards.
6. Close the upper steam supply and lower gas valve; open the lower steam supply and upper gas valve.
7. Steam for say one minute upwards.
8. Close lower steam supply and upper gas valve.
9. Open stack valve and turn on air supply.

This cycle of nine operations, occupying about five minutes, is repeated until it is necessary to recharge the generator with fuel. This is done when the level has fallen from say 7 ft. 6 in. to about 6 ft. during about six complete cycles. Finally, after about fifty-four cycles, it is necessary to remove clinker from the generator. This is done through the doors by means of long pokers.

A number of precautions are necessary in the operation of the plants. The most important are:

(i) The water gas enters the scrubber through a water seal so that gas from the main, which may be under pressure, cannot return to the hot generator during the blow periods or when charging or clinkering.

(ii) In order that the operations detailed under 4 and 6 above should be done simultaneously, the valves are linked together so that the operator has only one movement to make other than adjustment of the steam to the correct working pressure.

(iii) The main reason for up and down steaming is to maintain the fuel bed at a uniform working temperature and to keep the formation of clinker under control. After charging the generator with fuel, and after clinkering, it is necessary to steam upwards for one cycle in order to bring the new fuel bed to the working temperature. Otherwise the steam used in down running would come into contact with cold coke and a poor gas yield would result.

(iv) Before the top charging door can be opened to admit fresh coke the stack valve must be opened and the air turned on for a few seconds to sweep the space above the fuel bed free from water gas. If this is not done an explosion would result.

(v) For a similar reason an up-run must always precede a blow so that the bottom of the generator shall be full of steam; if it contained gas, as at the end of a down-run, the introduction of air would again cause an explosion.

(vi) When the time for "clinkering" the generator approaches it is customary to steam upwards for several cycles in order to cool the fire-bars and the lower part of the bed and facilitate working.

(vii) The water gas as it leaves the plant is scrubbed by a counter current of water in a special scrubber to free it from dust.

The first modification which was made to the above simple type of generator was the addition of a combustion chamber for burning the blow gases and a waste-heat boiler for the recovery of the sensible heat of the hot gases and the potential heat of the blow gas as steam which could be employed on the process. The arrangement is similar to that described below for carburetted water gas. The time cycle required a certain amount of modification in that the stack valve is now placed at the outlet of the boiler flues, and allowance must be made for the time taken by the gases to pass through the additional free space. For example, about eight seconds are allowed to elapse between the opening of the steam and gas valves and the closing of the stack valve when blowing. Additional complications are also introduced for the operator in the manipulation of air valves supplying the air for combustion of the blow gases in the heat exchanger.

A later modification is the introduction of water jackets for the generators to assist in heat recovery as steam.

In modern plants of large size the entire programme of operations is now carried out mechanically, the timing being controlled by an electrical timing device which controls all the operations including the charging of the coke at the correct intervals. Clinker discharge is made automatic and continuous by the use of rotating grates which crush the clinker and discharge it continuously through a water-seal or, in some cases, a specially constructed dry seal.

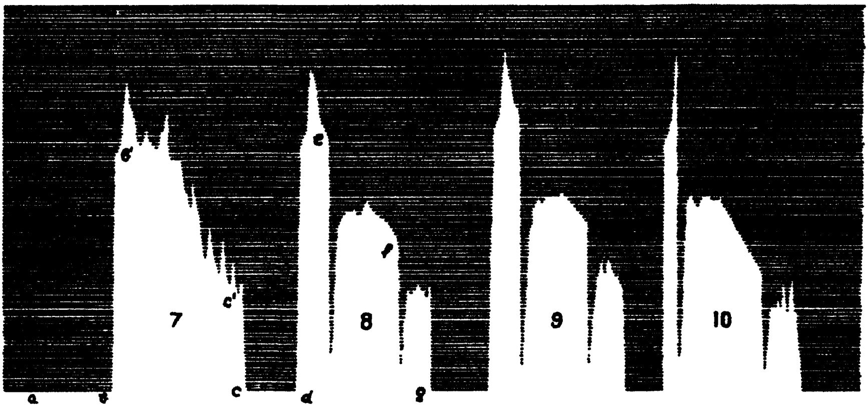


FIG. 53.—Variation of Rate of Gas Making in Water-gas Practice.

There are a number of factors which affect the yield of water gas, such as depth of fuel bed, rate of blow, working temperature, etc., but before considering these it is desirable first to have a clear idea of the nature of the variations which occur in the different parts of the water-gas cycle. The variations are best illustrated from the work of King and Shaw (Fuel Research Technical Paper 6, 1923), and King and Williams (Fuel Research Technical Papers 27 and 30, 1930).

The volume variations appear in a very interesting way when use is made of the photographic recorder of King and Williams (*loc. cit.*). A portion of a chart is shown in Figure 53. This is obtained as a record on a moving chart of the differential pressure on both sides of an orifice plate in the gas stream. The volume of gas is proportional to the square root of this pressure difference, so that after calibration of an instrument the area of the curves can be measured in terms of gas volume. This measurement is facilitated by the use of a square-root planimeter. The horizontal lines are spaced 1 mm. apart on the full-size records.

In Figure 53 the line *ab*, the base line, represents no gas flow, at *b* the gas begins to flow in the main and the differential pressure at the orifice is shown by the ordinate bb^1. As the rate of gas production falls off, owing to the endothermic nature of the reactions, the height of the ordinate decreases until, when steam is shut off at cc^1 it is less than half bb^1. During the interval *cd*, the fire is being blown and no gas is passing in the main. In the second cycle, *defg*, the direction of steaming is altered from upwards to downwards at *e* and then reversed at *f*. The momentary pauses caused by the change of direction of flow of gases in the generator are clearly seen. Further cycles repeat the same curves and the zero is continuously checked during the blows. The shape of the curves shows how the rate of gas-making decreases as the temperature of the fuel bed falls. In an extended run a general decrease would also appear in hand-clinkered plants owing to the accumulation of clinker.

The proportions of up- and down-running are variable and depend upon the nature and amount of the ash in the fuel. Generally they are chosen to keep the oxidation zone low and the clinker within reach; too much down-running would choke the grate with fused clinker. Figure 53, however, indicates that a study of the gas volumes produced in the corresponding parts of each cycle would facilitate an exact balance of conditions in cases where the ash was not of a difficult character.

It will have been realized that the composition and calorific value of water gas must vary, as well as its volume, during the stages described above. The scope of these changes is illustrated in Table LII, from results quoted by King and Shaw (*loc. cit.*). During the first one minute up-run gas is made at the rate of 571 cu. ft. per minute, during the down-run at 450 cu. ft., and during the last up-run at only 370 cu. ft. From beginning to end of a gas-making cycle the decrease in rate may be as much as 50 per cent.

The thermal balance of operations in a simple water-gas generator may also be illustrated from King and Shaw. Their results are shown in Table LIII, and yield the following conclusions regarding a water-gas generator in which there is no recovery of heat from the hot gases.

(i) The heat available in the water gas produced is not more than 60 per cent. of that in the fuel and steam used.

(ii) The proportion of heat lost from the system in the hot gases is very high, over 30 per cent.

(iii) The loss of unburned fuel is high, about 5 per cent.

TABLE LII

RATE OF PRODUCTION AND COMPOSITION OF WATER GAS AT DIFFERENT STAGES
In a Generator Producing 500,000 cu. ft. per day

	During first up-run.	During down-run.	During final up-run.	Average.
Gas volume, cu. ft. per min.	571	450	370	436
Gas composition :				
CO_2	2·2	2·3	9·0	4·5
CO	45·8	43·6	39·4	41·6
H_2	47·0	52·5	51·0	50·5
CH_4	0·3	0·4	0·1	0·2
N_2	4·7	1·2	0·5	3·2
Gas calorific value, B.Th.U. .	298	310	290	296
Maximum temperature of gases leaving generator—deg. C.	670	440	600	Blow gas 780

Blow gas	CO_2	CO	H_2	CH_4	N_2
	14·6	9·3	3·7	0·8	71·6
Calorific value . . .	49 B.Th.U. per cu. ft.				

TABLE LIII

THERMAL BALANCE OF WATER-GAS PROCESS
Percentages of Heat to Generator

Coke	92·52	Water gas, potential . .	57·81
Steam	7·35	„ „ sensible . .	3·23
Air	0·13	Blow-gas, potential . .	18·95
		„ sensible . .	9·33
		Clinker and ashes, potential .	2·28
		Unburnt coke, potential .	2·26
		Dust, potential . . .	0·33
		Sensible heat of last three .	0·33
		Water vapour . . .	2·13
		Difference, including radiation, etc., losses . .	0·07 3·28
	100·00		100·00

So far as yields are concerned the following figures emerge from the same data :

	cu. ft.
Gas produced per lb. of dry, ash-free coke	30·1
„ „ „ „ steam	30·3

These figures are useful for calculation purposes either as quoted or in terms of the amounts required to produce 1000 cu. ft. of water gas ; these are 33·2 lb. coke and 33·0 lb. steam respectively.

The large losses of heat from the system in the hot gases has led to the development of waste-heat boilers and recuperators and regenerators. *The former were not at first popular, but the original difficulties have now been overcome and all the larger plants now employ water jackets* on the generators and waste-heat boilers. Steam recovery figures for a carburetted water-gas plant have been quoted of 73 lb. per 1000 cu. ft. of gas at a pressure of 95 lb. per sq. in. This represents a boiler efficiency of about 45 per cent. Owing to the fact that this steam would have been raised by coke breeze and not by lump coke, this does not represent a corresponding saving of coke.

Operating figures for a large modern water-gas plant are quoted in *Engineering* (1929, March 22). The plant embodies generators of 10 ft. internal diam. by 13 ft. high, each of which makes 1·9 million cu. ft. per day at a mean calorific value of about 295 B.Th.U. This represents 67,000 to 70,000 cu. ft. of gas per ton of coke containing 10 per cent. of ash and 5 per cent. of moisture. Steam raised by the boilers amounts to 96 lb. per 1000 cu. ft. of water gas made.

Important Factors in Water-Gas Practice. It will be realized from the above that the important factors in the obtaining of a good thermal yield in water-gas manufacture are (i) the storage of heat in the fuel bed in the minimum time and with the minimum loss, and (ii) the efficient utilization of the heat thus stored. Provision (i) can be attained by increasing the efficiency of the blow, assuming that the final temperature cannot be raised beyond a certain point determined by the fusibility of the ash. This can be done by blowing as completely as possible to CO_2, either (*a*) by using a shallow fuel bed, as in the old Dellwik-Fleischer process, or (*b*) increasing the rate of blowing. The first alternative reduces the output of a given plant, and the second seems more desirable, the time of blowing being reduced correspondingly with increase of rate so that the mean temperature of the fuel bed remains the same. The limits imposed on this alternative are the practical ones of cost of high-pressure fans and disturbance of the fuel bed.

King and Shaw (*loc. cit.*) have reported experiments with a shallow fuel bed in a Humphreys and Glasgow generator rated at 500,000 cu. ft. per day.

Fuel bed—ft.	3·0	3·5	4·0	7·0
Thermal efficiency, per cent.	54·7	57·8	59·9	57·8
CO_2 in blow gas, per cent. . .	19·5	19·0	19·1	14·5
Gas made per day, cu. ft. . .	237,000	230,000	219,000	378,000
Heat lost by radiation, etc., per cent.	11·8	10·6	11·2	3·3

The above results show that a higher thermal efficiency is obtainable in this way despite the higher proportional losses due to radiation, etc., which are the result of lower output.

In later experiments the increase of efficiency possible by increasing the rate of blowing is clearly shown:

	1.	2.	3.
Rate, cu. ft. air per minute	4,780	2,300	1,400
Volume of air per blow	802	997	1,167
Efficiency of blow	86	84	61
Efficiency of process (therms water gas per 100 therms coke)	76·8	72·4	68·7

Small increases in efficiency can be assured by finding the optimum conditions for the rate of passage of steam through the fuel bed. In British practice the normal efficiency in steam decomposition is about 70 per cent.

Temperature of Operation. The higher the temperature range over which the fuel bed fluctuates, the higher will be the thermal efficiency of the process and the better the water gas produced. The normal range is about 250° C., i.e. 1400° C. at the end of the blow and 1150° C. at the end of the run. King and Williams (Fuel Res. Tech. Paper 30, 1931) have shown that, by reducing the output of a generator until the temperature range is such that clinker troubles are prevented an increase of efficiency of as much as 20 per cent. over normal conditions is possible.

Industrial Applications of Water Gas. The chief use of water gas is in its carburetted form (see below) as a substitute for coal gas for towns' purposes. "Blue" water gas is, however, of special service in many heating operations. Its gross calorific value is about 310 B.Th.U., and net 280 B.Th.U. per cu. ft. The gas is capable of giving a very high flame temperature. According to Roessler, with pre-heated air a temperature well above the melting-point of platinum (1780° C.; 3236° F.) is attained; under ordinary conditions of combustion the hottest part of the flame is from 1530–1645° C. (2800–3000° F.).

For furnace heating, where the work is intermittent and quick heating is desired, water gas has the advantage over ordinary producer (mixed) gas. It has been used to a limited extent in steel furnaces, but here producer gas—used hot and with its tar vapours—with its simpler production, continuous make, and less costly plant is more generally advantageous. For furnaces for heating drop forgings and stampings and such class of work, it is employed, and to a limited extent for metal melting. Plant is, however, unlikely to be installed specially for these uses.

Water gas is, however, valuable for special welding processes, especially for steel mains and pipes. According to Meade, the burners for this purpose are supplied with gas at half a lb. pressure, the air at 2¼ lb., the consumption per burner being 9000 cu. ft. per hour. A steel main 18 ft. long and ½ in. thick can be welded along the joint *in about one hour. The same writer states that water gas is used* also for glass melting and for cement kilns.

Water gas is not normally used for power production in gas engines, owing to its high percentage of hydrogen and the resulting tendency to pre-ignition. The higher percentage of water gas to give an explosive mixture with air is 57 ; the lower limit, 12·5 per cent.

One of the most interesting developments in the use of water gas is in the production of pure hydrogen. For this gas there are very large demands to-day, principally for the synthetic production of ammonia by combining the hydrogen with atmospheric nitrogen. Hydrogenation processes for the treatment of coal and tars are under development and have already been described (Ch. VIII). The hydrogen may be obtained directly from the water gas by the usual processes of liquefaction, carbon monoxide being the more easily liquefied gas. The more general method, however, involves the well-known action of iron on steam at a high temperature. Spathic iron ore is reduced by the passage of water gas over it at about 760° C. until its surface is metallic iron. This reduced surface then serves to convert steam into hydrogen, the iron becoming again oxidized. The process is operated on a time cycle similar to that of the water-gas process. From 2 to 2·5 volumes of water gas are consumed per volume of hydrogen produced and the latter may easily have a purity of over 99 per cent., the impurities being carbon monoxide and nitrogen.

Carburetted Water Gas. "Carburetted" water gas is a substitute, for towns' purposes, of coal gas. One important point in its use is the rapidity with which the plant can be brought into operation to supply sudden demands. This flexibility is an important reason for the wide use of plants for its manufacture.

The generator and its system of valves are the same in a carburetted water-gas system as for simple or "blue" water gas. The additional plant necessary are the carburettor for vaporizing the enriching oil and the superheater for cracking the vapour to permanent gas.

The general arrangement of a modern plant is shown in the frontispiece and also in section in Figure 54. The generator has a boiler jacket, mechanical grate and automatic controls on valve operation and coke feed. The carburettor is a cylindrical brick-lined chamber filled with chequer work over which the enriching oil is sprayed. In Figure 54 the carburettor is of a special type and does not contain chequer brickwork, but two ignition arches are sprung across the carburettor. The oil is sprayed upwards from four nozzles spaced round the circumference as shown and directed upwards at an angle of about 30° so that the oil travels against the gas stream. Oil may also be sprayed into the dome of the generator over the fuel bed.

The superheater is similar to the carburettor and in it the oil vapour carried by the water gas is cracked to permanent gas.

The plant is operated as for water gas. During the blow the carbon monoxide in the gases is burned with air in the carburettor and superheater, raising these chambers to the working temperature. When water gas is being made oil is admitted to the carburettor immediately after opening the steam valve. The oil is vaporized, leaving some coke in the chequer work. The oil supply is checked before the end of the run so as to make sure that all of it is vaporized before the next blow. During the blow the residual carbon is partly burned off. The necessity for fairly frequent cleaning out has resulted in the design of plain chambers such as in Figure 54.

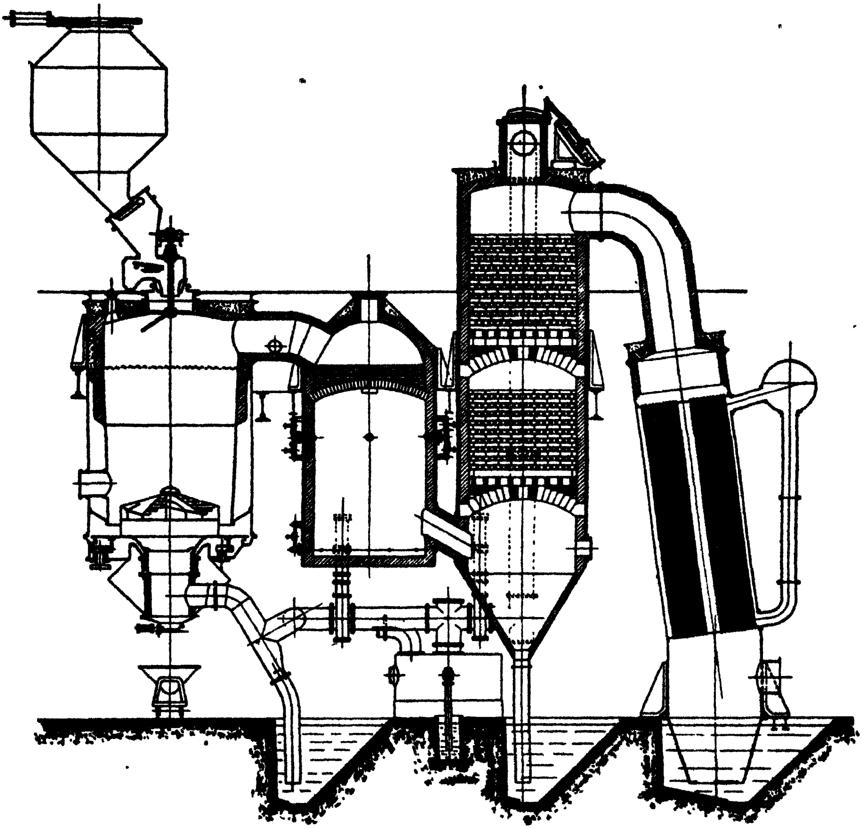


Fig. 54.—Carburetted Water-gas Plant.
(*Power Gas Corporation*).

The correct temperature for cracking the oil is approximately 730–760° C. in the superheater. The temperature in the carburettor tends to vary widely (1000–600° C.), but this is less important. The time of contact of the gases with the hot surfaces may vary from one to ten seconds without much change in efficiency of cracking. The oil normally used is petroleum "gas oil" (boiling range 200–300°). The amount of oil used depends upon the degree of enrichment required. In good practice the cracking of one gallon of gas oil will yield 70 cu. ft. of gas having a calorific value of about 1550 B.Th.U. per cu. ft. In order to raise the calorific value of water gas from 295 to 500 B.Th.U. it would therefore be necessary to crack over 2 gallons of oil per 1000 cu. ft. of carburetted gas made. This represents an efficiency of cracking of about 75 per cent., the remaining 25 per cent. being accounted for as carbon deposited and as heavy unvaporized residue which is collected from the system as water-gas tar. This tar may amount to about 15 gallons per 100 gallons of oil cracked. A portion of the oil vaporized is present in the gas as condensible, rather than gaseous, hydrocarbons. This may amount to 10 per cent. of the oil gasified.

The thermal balance of the combined process, water-gas generation and oil cracking, can be illustrated from the work of the Institution of Gas Engineers (7th Report, 1922).

THERMAL BALANCE OF CARBURETTED WATER-GAS MANUFACTURE

Coke	57·3	Gas, potential heat	60·2
Oil	38·5	sensible heat	4·0
Air	0·1	Steam, undecomposed	1·9
Steam	4·1	Tar, potential heat	6·5
		sensible heat	0·3
		Blow, gas, potential heat	12·9
		sensible heat	6·3
		Clinker and ash	4·2
		Radiation, etc.	3·7
	100·0		100·0

In this case the calorific value of the gas was 485 B.Th.U. per cu. ft. and the amount of oil sprayed amounted to 1·854 gals. per 1000 cu. ft. of c.w.g. made. The efficiency of gas production was 67·1 per cent.

The Cleaning of Water Gas. The gases leaving the generator of a water-gas plant contain water vapour, sulphur compounds and dust. The dust in particular must be carefully removed to avoid trouble with valves and mains. This is done either by means of baffled dust traps followed by counterflow water washers and finally, if very efficient cleaning is desired, by centrifugal cleaners. Such treatment removes only a small proportion of the hydrogen sulphide, and this must be removed by the usual iron oxide method. Normal amounts are 70–80 grains per 100 cu. ft. of gas.

In the manufacture of carburetted water gas the position is complicated by the presence of tar from imperfectly cracked oil, and tar extractors and separating tanks are added to the system.

Variations in Carburetted Water-Gas Practice. Generally speaking, the variations which are possible in making carburetted water gas are less than in making simple water gas. It is essential that the temperature of the cracking surface be maintained at the right level so that other conditions must be arranged to suit. The higher the calorific value aimed at, the greater is the volume of oil to be cracked and the generator must have a higher temperature in order that the blow gases will contain more carbon monoxide and provide more heat on combustion.

Two variations of the water-gas process, the back-run and the down-run, are employed to increase the efficiency of operation. In the Chrisman down-run process the relatively cool down-run gases are by-passed so that they do not cool down the carburettor and superheater. The necessary oil-cracking is, in this process, all done on the up-run gas which leaves the generator at a higher temperature. It has been estimated that this simple change reduced the fuel consumption by 2 to 3 lb. per 1000 cu. ft. of water gas made. It will be apparent that the generator efficiency is not increased by this modification.

The Back-Run Process. In this process the steam for the down-run is introduced at the top of the superheater, thereby cooling the brickwork so that the blow gases which follow do more work and leave the system at a lower temperature. The down-run gas, as in the Chrisman back-run, is not carburetted and all the enriching is done on the up-run gas. This modification is stated to reduce fuel consumption by about 3 lb. per 1000 cu. ft. of gas made. Most of the saving is effected by the return of heat from the superheater to the generator and lower rate of cooling of the fuel bed. One disadvantage is the loss of steam when the superheater is swept by the up-run which follows the down-run.

Full details and comparisons of back run and down procedure can be found in the excellent paper by the 31st Research Committee of the Institution of Gas Engineers, 1932. The plant used was by Humphreys and Glasgow, and had a rated capacity of 1·75 million cu. ft. of gas of 500 B.Th.U. per day. The following are important data, quoted from the report, for carburetted gas of 490 B.Th.U. :

	Back-run.	Down-run.
Coke consumption, lb. per 1000 cu. ft. . .	41·9	41·3
Steam to generator " " " " " . .	41·2	40·4
" " plant " " " " " . .	41·3	42·2
Total " " " " " . .	82·5	8·26
" raised in annular boiler . . .	36·4	38·3
" raised in waste-heat boiler . . .	86·5	87·3
Oil . . . . gals.	2·44	2·24
Efficiency per cent. of production of water gas .	48·0	49·1
" " " " " " carburetted gas	68·8	68·5

Composition of carburetted gas:	Back-run.	Down-run.
CO_2	3·7	3·7
C_nH_m	7·4	7·5
O_2	0·4	0·5
H_2	37·3	36·5
CO	34·8	35·5
CH_4	9·0	8·6
C_2H_6	1·5	1·6
N_2	5·9	6·1
B.Th.U.	494·7	491·2

The Use of Oxygen. If a cheap supply of oxygen were available it would be possible to operate the water-gas process without the blow period by using a mixture of oxygen and steam. So far this modification of the process has not progressed beyond the experimental stage. Since the temperature of the generator must be kept below the slagging temperature of the ash, the output tends to be low and the proportion of carbon gasified to CO_2 high. Using a blast consisting of 3 volumes of oxygen to 7 volumes of steam, it is reported that the water gas has the composition, CO_2 13·2, O_2 1·1, CnHm 2·3, CO 32·9, H_2 42·8, CH_4 1·1 and N_2 6·6. It has been calculated that, for this purpose, commercial oxygen would have to be available at about 1*s*. per 1000 cu. ft.

An alternative method of supplying the endothermic heat of reaction of the run so as to obtain a continuous process is to heat the generator externally. This alternative offers greater promise and a gas of higher calorific value, but so far has received comparatively little attention.

OIL GAS

Oil gas is made by the cracking or thermal decomposition of oil as in the enrichment of water gas. In the United States, in certain districts where oil is cheap, the oil gas is distributed as a towns' gas. In this country its chief application is in isolated positions. Several types of process are available which give satisfactory yields. In the Dayton process a cracking chamber is heated externally by oil burners and a mixture of gas and air atomized into the chamber. It is possible to vary the calorific value of the gas from 300 to 560 B.Th.U. per cu. ft. conveniently. The consumption of oil is about 4 gals. per 1000 cu. ft. of gas of 450 B.Th.U., and its cost in the U.S.A. is stated to be about 35 cents. The thermal efficiency of the process is about 75 per cent. to gas, while about 8 gals. of tar are produced per 100 gals. of oil cracked. Careful control of the conditions of cracking is necessary in order to avoid the accumulation of carbon in the retort.

THE COMPLETE GASIFICATION OF COAL

Processes for the complete gasification of coal are the direct result of attempts to manufacture water gas with coal as the fuel instead of coke. In the early days of water-gas plants coal and anthracite were used, but these soon gave place to coke. During the last ten to fifteen years the use of coal has been revived, particularly in the United States, and modified processes are now available which are both efficient and practical.

In a water-gas generator the obvious difficulties which the use of coal gives rise to are those caused by the caking of the coal, swelling and sticking in the generator, resistance to the passage of the gases, etc. The tar carried by the gas is another source of trouble in the operation of valves, especially as the tar fog is present in the blow gas as well as in the water gas. When using coal the blast pressure is generally lower, the output of the generator less by perhaps 30 per cent., and amount of fuel used for a given output of gas greater by about 10 per cent. Sometimes the gas made in the last portion of the blow is passed to the wash-box since it is rich enough not to dilute the water gas too much. A modification of the generator is due to Murdock, Evans and Lungren (Amer. Gas Assoc., 1925), who introduce a brick pier into the coal bed so that the rate of heat transfer is increased by disturbing the central plastic zone. Output and yield are both increased as a result.

	With pier.	Without pier.
Fuel, lb. per 1000 cu. ft.	37·2	41·2
Output	144	100

The use of coal in this way is obviously wasteful since too high a proportion of the coal gas is lost in the blow gas. The idea of using the sensible heat of the water-gas process to carbonize coal has, however, given rise to complete gasification proper where the coal is treated in two zones, the blow gas leaving the system at the top of the gasification zone. Since the sensible heat of the water gas is insufficient alone to carbonize the coal in the carbonization zone, heat must be supplied either externally or by superheating the water gas or by using the potential heat of the blow gases to heat the carbonization zone.

The advantage to be gained by gasifying coal in a single process rather than by combining coal carbonization with a water-gas plant can be illustrated by the following yields per ton of coal:

		Therms.
Coal gas, 13,400 cu. ft. at 560 B.Th.U.	=	75·0
Water gas, 30,000 cu. ft. at 296 B.Th.U. .	=	88·8
		163·8
Complete gasification (Humphreys and Glasgow): 53,720 cu. ft. at 340 B.Th.U.		182·8

In making the comparison it is assumed that 3 cwt. of coke per ton of coal are required for carbonization purposes, that 10 cwt. remain for treatment in the water-gas generator, and that the latter recovers from waste heat all the steam necessary for running it.

Against this gain of 12 per cent. there is the loss of tar since the coal is not completely carbonized when it reaches the gasification zone. The complete gasification plant should take up less space, involve less capital expenditure and use less labour. Its most important implication is the complete consumption of coke, and from this point of view the partial utilization of the process in gas manufacture should be of importance as a means of balancing coke demand and supply in outside markets.

Most of the plants for complete gasification consist essentially of a carbonization chamber situated above a water-gas generator; gases from the blow period are burned in chequer-brick chambers round the carbonization chamber and provide the heat necessary. The water gas passes upwards through the carbonization zone, providing more heat for this purpose, and mixes with the coal gas formed. The best known processes are the Tully, Mond, Strache and Kraemer and Aarts. In this country Tully plants are in operation in 30 to 40 gasworks.

The Travers-Clark system (*J.S.C.I.*, 1928, **47**, 203), is rather different in principle. The blow gases pass from the gasification zone to a separate regenerator where they are burned with air. During the run part of the gas made is drawn back through the heated regenerator and carries its heat through the coal charge, thereby effecting carbonization. Griffith (*Manufacture of Water-Gas*, Ernest Benn, Ltd.) quotes the results of test work on a Travers-Clark plant (quantities per ton of coal):

Uncarburetted gas, cu. ft.	41,900
„ „ therms	150·7
Oil for carburetting, gals.	58·8
Carburetted gas, cu. ft.	45,900
„ „ therms	204·5

The efficiency of the process is quoted at 55·3 per cent., including steam for the auxiliary plant or 65·2 therms of gas per 100 therms of coal gasified.

In the Humphreys and Glasgow plant, the most recent type in this country, the regenerator is replaced by the carburettor and superheater of a normal carburetted water-gas plant. The plant (Figure 55) consists of a water-gas generator with a superimposed carbonizing chamber. The blow gases leave the generator via an annular chamber surrounding it and are burnt in the carburettor with secondary air, storing heat therein and in the superheater. During part of the run the coal in the carbonizing chamber is carbonized by the sensible heat of the water gas resulting from a modified back-run produced by admitting steam to the superheater top and leading the superheated steam to the generator base. In another part of the run the coal is carbonized by the sensible heat of the up-run gases made from steam not superheated in this way. Since this sensible heat is not sufficient for the purpose additional heat is returned from the superheater and carburettor by circulating some of the gas made during the back-run along with the usual back-run steam. Simple adjustment of the amount of re-circulation gives complete control of the carbonizing zone and ensures a properly carbonized coke for the water-gas zone. During the time the fixing vessels are not being used to superheat steam they are used, as in normal carburetted-gas practice, for cracking the oil necessary for enrichment to a desired calorific value. A certain proportion of down-running is used; the minimum necessary to bring the clinker down to the grate.

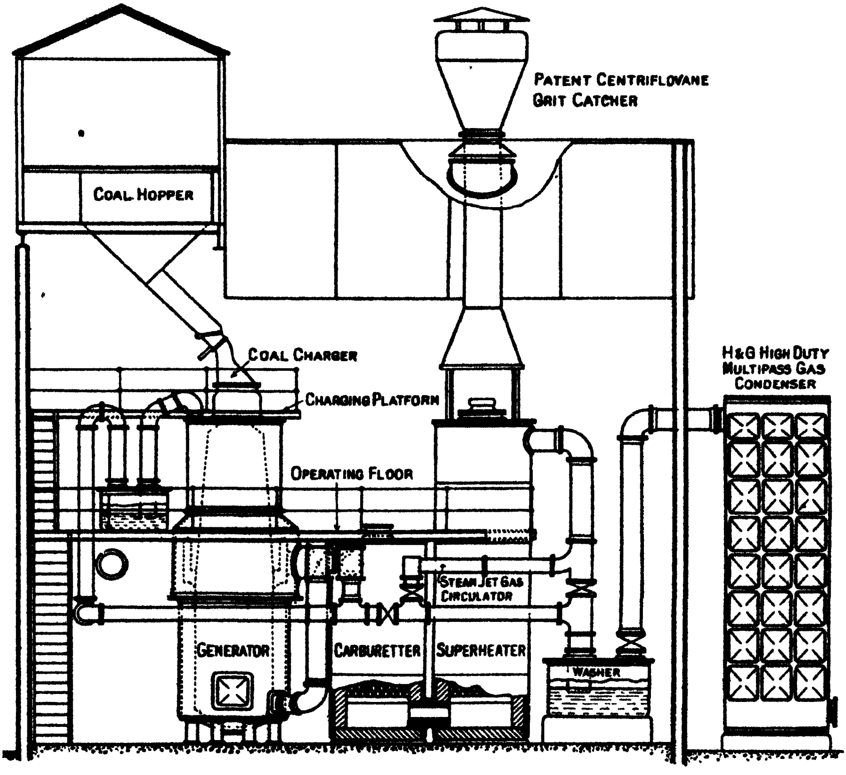


FIG. 55.—Humphreys & Glasgow Complete Gasification System. Coal-carburetted Water-gas Plant.

The first plant of this type was installed in 1926, with a capacity of 800,000 cu. ft. per day. It has shown that it can deal with Yorkshire caking coals, Durham gas coals, and blended smalls. The thermal yield is about 180 therms per ton of coal without addition of oil. The following yields are quoted (*Gas J.*, 1933, **204**, 643) of a test on South *Yorkshire gas nuts:*

Coal (dry), per day, tons	12·9
Gas per ton of dry coal, cu. ft.	53,720
" " " " , *therms*	182·8
Gas calorific value, B.Th.U.	340

The composition of the gas is approximately CO_2 6·2, CnHm 0·8, CO 28·0, H_2 48·0, CH_4 7·0, N_2 10·0.

Further carburetting of the gas to the desired calorific value is, of course, achieved at the normal efficiency of this process. The plant as a whole is a flexible addition to gasworks equipment, being able to operate as desired on coal or on coke, to take peak loads, or render more coke available for sale.

The possibilities of the alternative procedure in which the carbonizing zone is externally heated are brought out by Barash and Tomlinson (*J. Inst. Fuel*, 1932, **5**, 333), who steamed so heavily during carbonization in a Glover-West retort that no coke remained for sale, that produced being only just sufficient to run the producers and ancillary plant. Using Wigan Arley coal (ash 7·5, moisture 2·6 per cent.), which on carbonization in the normal way gave a yield of 13,000 cu. ft. of gas at 540 B.Th.U. or 70·2 therms, a yield of 53,180 cu. ft. or 191·4 therms at 360 B.Th.U. was realized with excessive steaming to about 100 per cent. by weight of the coal. Of the 13 cwt. of coke normally produced, the yield was reduced to about 6·5 cwt., all of which was required to supply the extra heat required for carbonization. The gas yield is not dissimilar to that quoted above for the Humphreys and Glasgow process, and it is suggested by the authors that the process deserves consideration in more than one set of circumstances in gasworks practice. The residual coke is not necessarily of very high ash content, since the ash of the consumed portion can be removed from the remaining lumps by screening. In this case the residual coke contained only 17·6 per cent. of ash and was quite suitable for the producers.

CHAPTER XVI

PRODUCER AND BLAST FURNACE GAS

PRODUCER GAS (AIR-COKE GAS, SIEMENS GAS)

The gas resulting from the action of air only on highly heated carbon, and therefore consisting essentially of carbon monoxide with a large volume of inert nitrogen derived from the air, was the first form in which "gasified" carbon was applied in practice. Bischof (1839) introduced a simple form of producer, open to the air at the bottom, through which the air current was drawn by natural draught.

The development in the use of gasified fuel was associated closely with improvements in metallurgical furnaces with regenerative working, which the brothers Siemens introduced and developed. In the earlier forms of producer the fuel was gasified by an air current induced by natural draught; later, Siemens used a closed bottom producer, water being kept in the ash pit and air blown in; still later, a steam injection system for carrying in the air was introduced.

The composition of the gas obtained by the action of air alone should be approximately one volume of carbon monoxide and two volumes of nitrogen; its relation to the other fuel gases, average composition, etc., is given in Table III, Appendix. It has been shown that the "cold gas" efficiency of such a producer would be about 70 per cent.; by using the gas hot efficiencies of from 80 to 85 per cent. may be attained.

The composition of the gas obtained from a bituminous fuel partook naturally of the character of a mixture of producer gas proper and the gases distilled from the coal. The composition of a Siemens gas produced from bituminous fuel in a wet-bottom producer was:

	per cent.
Carbon monoxide	23·7
Hydrogen	8·0
Methane	2·2
Carbon dioxide	4·1
Oxygen	0·4
Nitrogen	61·6

The use of simple producer gas was confined entirely to metallurgical operations. With the knowledge of the advantages of the joint action of air and steam the production of this simple gas soon ceased, and "mixed" gas is now employed invariably.

"MIXED GAS" (SEMI-WATER GAS, DOWSON GAS)

It has been shown already that by the joint action of air and steam on carbon a mixed gas, consisting partly of the producer gas proper and water gas, may be made by a *continuous* process. This offers obvious advantages over any intermittent process.

The wonderful development in the use of these poorer gaseous fuels, the production of which led naturally to a simultaneous improvement in gas engine design and operation, formed a marked feature in industrial progress at the end of the twentieth century. Reference has been made already to some of the advantages gaseous fuels of this character offer. In the early years of its introduction for power and other purposes, the successful results obtained were due largely to the skilful handling of the problem by Dowson, who in 1881 demonstrated the value of poorer gases in a 3 H.P. Otto engine. The later development of large gas engines, working at high compressions on these poor gases, and the application of these engines to the efficient utilization of waste gases, or gases hitherto inefficiently utilized, as blast furnace gas, must be attributed in the main to his pioneer work.

Pressure and Suction Plant. The gasification of the fuel is carried out in cylindrical producers, in which an air-steam current acts upon the carbon of the fuel. The producers may be worked under pressure, the air being forced through either by a steam jet or by a fan blower. The natural development was to make the suction stroke of the engine itself pull through the necessary air-steam mixture, giving the well-known suction gas plant. The nature of the gas produced from a given type of fuel obviously will be almost identical for the same conditions of air and steam supply.

In general, the pressure plant is more particularly suited to the production of large quantities of gas, and is adopted almost universally where gas is required for both power and heating purposes. More recently special forms of such plant, in which air-steam is drawn through by a fan and the gas distributed much as with pressure systems, have been designed, but their advantages over the pressure system are not very obvious, beyond reduction of the risk of carbon monoxide poisoning should a leak occur. Working under suction, gas cannot escape outwards; any leakage will be of air inwards.

The suction plant is suited more particularly to power production on a small or moderate scale, and generally the gas producer, gas cleansing arrangements and engine form a complete unit.

Until about ten years ago a considerable proportion of industrial power was raised by suction-gas plants, but to-day the increased efficiency of steam plants, the extending use of the heavy oil engine and electricity distribution by the "grid," have reduced their use to small units in special circumstances.

Fuels for Gas Producers. Since the regular flow of gas through a bed of fuel is an important factor in the process it is apparent that the type of fuel most suited is that which does not coke or cohere and which allows free passage of the gases. Such fuels are anthracite and coke. The design of the auxiliary plant will be least complicated the purer the gas as it leaves the producer; the simplest form then will be for plant utilizing anthracite or coke. The advantage of being able to work with bituminous coals of lower cost is obvious, but their use entails greater complication in design, higher first cost and working expenses, where the gas has to be used in engines. The tar vapours may be advantageous in metallurgical operations, by reason of their adding to the calorific value of the gas. In this case the gas passes as directly as possible from the producer to the furnace, and its sensible heat also is utilized. In general, bituminous fuels are best treated in pressure plant, although several forms of suction plant work successfully on certain types of bituminous fuel.

The variety of fuels which have met with successful application in gas-producer practice covers pretty well all carbonaceous materials, ranging from high-class anthracite to colliery refuse containing over 50 per cent. of ash, quite useless for fuel in any other way; it includes lignites, peat, wood waste, spent tan, coco-nut shells, etc.

In the case of coals the chief limiting factor is caking power since caking coals tend to form crusts which crack and form channels through which the air and steam pass too readily. The ratio of hydrogen to oxygen in producer coals should normally be less than 0·55. Since high-volatile coals are often non-caking the maximum enrichment of the gas is conveniently obtained by using non-caking coals of 35–40 per cent. volatile matter. Non-caking or weakly caking coals are, however, equally convenient as regards the operation of the producer. Producer coal should preferably be carefully sized and in particular should contain the minimum of dust. The choice of size will depend upon price but, other things being equal, a 1½–½ in. fuel is the most satisfactory. It may be taken that actual size is, however, less important than close grading. A good producer fuel should not cover a wide range of size since this causes inequalities of draught. Owing to their cheapness, non-caking slacks are very frequently used in producer practice although the presence of the fines leads to lower efficiency.

The ash of producer coals should be non-fusible at the working temperature. In the best class of coal a fusion temperature of over 1400° C. ensures absence of clinkering and a high gas output. Too high a moisture content is also unsatisfactory in that this moisture has to be evaporated in the top of the producer, causing a high sensible heat loss and also in that the steam causes oxidation of the carbon monoxide of the gas with a consequent loss of calorific value and potential heat.

Formerly, before the coming of synthetic ammonia, plants for the recovery of ammonia were attached to certain types of producer plant (e.g. Mond). In these days the nitrogen content of the coal was of importance, as much as 70–80 lb. of ammonium sulphate being obtainable from a ton of suitable coal.

General Considerations. On theoretical grounds it has been shown that a temperature of about 1000° C. is requisite for the production of gas with low carbon dioxide content. The temperature attainable in practice is limited by the durability of the lining of the producer, but more especially by the liability to form clinker from the ash of the fuel. The question of fusibility of coal ash has been referred to on page 53. Unless the gas is used hot, high temperatures in the producer lead to big losses of sensible heat in the gases, and low thermal efficiency results.

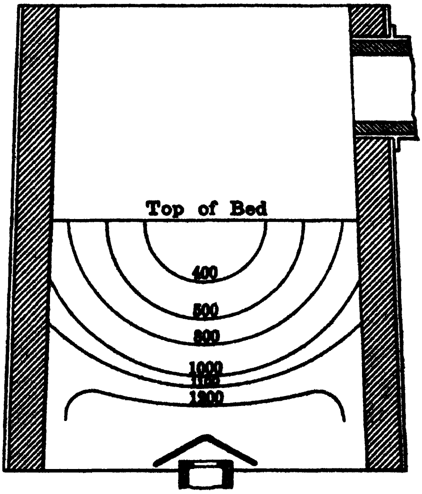


FIG. 56.—Diagram of Temperature Distribution in a Gas Producer.

Clement and Grine (U.S. Geol. Surv. Bull., 393, pp. 15–27) give the results shown in Figure 56, with a producer 6 ft. 6 in. diameter at the top, 7 ft. at the bottom, and with a fuel depth of 8 ft. 6 in. The maximum observed temperature was 1300° C. (2370° F.). It will be seen that the temperature towards the centre was much lower at a given height than at the sides, and this was ascribed to a badly designed tuyère. Proper distribution of the blast through the fuel is an important question.

In a Taylor producer, Pennock (*J.S.C.I.*, 1905, 600) obtained the following temperatures above the fuel bed:

At top of fuel	950–970° C. (1740–1780° F.).
2 in. above surface	900–910° C. (1650–1670° F.).
1 ft. above surface	650–660° C. (1200–1220° F.).
2 ft. above surface (at outlet)	595–605° C. (1100–1120° F.).

The temperature conditions in a suction producer were investigated by Garland and Kratz; they found a maximum temperature of 1315° C. (2400° F.) in the fuel bed 12 in. from the grate and an exit gas temperature of 600° C. (1110° F.).

It has been shown also that steam is the temperature regulator, and it follows that the character of the fuel, both its moisture content and the character of the ash, plays an important part in determining the air-steam ratio demanded.

The quantity and character of the ash of the fuel is of very great importance. If the ash is fusible, in order to prevent formation of troublesome clinker, a high steam ratio has to be employed in order to keep a lower temperature and so avoid excessive clinker formation. This leads necessarily to impoverishment of the gas. Much clinker entails considerable labour in keeping the producer working under good conditions, and where a grate which actually supports the fuel bed is employed the ash and clinker interfere seriously with the free passage of the blast. In producers where the ash does not rest on a grate, little trouble is experienced with fuels having quite a high ash content, if the ash is not of a very fusible character. With suitable producers the gasification of colliery waste, etc., containing up to 50 per cent. of ash, material quite unfit for use as fuel in any other way, can be readily accomplished.

Producers for such fuels usually are constructed to work under a higher blast pressure than ordinarily; in many the water-sealed bottom is replaced by a closed-in bottom, and special mechanical arrangements provided for removal of the ash and clinker.

The rate of gasification is one of the most important factors in producer practice; for a given consumption it determines the number to be installed. There comes a natural limit to the rate by reason of the very high temperature attained at high blast pressure, with consequent formation of clinker, especially with fuels of high and fusible ash content. The usual rates of gasification vary between 10 and 30 lb. per sq. ft. per hour. In slagging producers, where steam is not used and the ash is removed in a molten state the rate may be as high as 100 lb. In a powdered fuel slagging producer a rate as high as 160 lb. has been reported.

Ratio of Air to Steam. The graphs shown in Figure 51, Chapter XIV, show that the calorific value of producer gas reaches an optimum when the air supply contains about 0·4 lb. of steam per lb. of fuel. Since undecomposed steam is an undesirable diluent in producer gas and reduces efficiency both in production and combustion it is normally desirable to inject rather less steam than this, say 0·35 lb. In certain cases it may be desirable to increase the steam ratio to 0·6 lb. if the ash of the fuel tends to clinker and continuous operation cannot be maintained.

In ordinary producer practice even higher amounts of steam are common. It is commonly assumed that the additional fuel required under the boiler is one-sixth the weight of fuel gasified.

In pressure plant the air may be injected by means of a steam jet, or, usually in the larger plants, by a fan or blower, when it takes up the requisite steam from water maintained at a suitable temperature. Insufficient attention is paid in many injectors to providing easy control of the air-steam ratio. With a fixed steam jet and open air orifice variation is possible only by alteration of the steam pressure. A steam jet directed into a cone and capable of moving in and out will enable the ratio to be adjusted, or, in other cases, provision is made for excess air to be the normal condition, the actual admission being regulated by adjustable louvres. Annular steam jets are more efficient than " solid " jets.

In pressure plants operated by a blower, and in most suction gas plants the ratio is dependent on the saturation temperature of the air by steam. On theoretical grounds it may be calculated that, with conditions of air and steam supply properly balanced for thermal equilibrium with the production of carbon monoxide and hydrogen only, each pound of carbon gasified requires 42 cu. ft. of air and 0·64 lb. steam, calculating the steam as water. If the steam is supplied as such the air requirement is less, 29 cu. ft. and 0·75 lb. steam. In actual practice heat is lost in other ways than by the endothermicity of the steam-carbon reaction and the practical figure of 0·4 lb. of steam per lb. of fuel (see above) is approached. The proportion of steam to air is calculable from the saturation temperature. The curves given in Figure 57 show the weight of 1 cu. ft. of air at different temperatures, and the weight of steam 1 lb. of air can carry at saturation at various temperatures.

The steam supplied should be dry; wet steam clearly leads to greater cooling than a corresponding quantity of dry steam, hence when dry it is equivalent to the producer taking a greater proportion of steam, thus yielding a higher proportion of water gas in the " mixed " gas, with corresponding decrease in the volume of non-combustibles. Superheating is clearly an advantage, and since this can be arranged for by utilizing sensible heat in the gases produced, this heat is conserved. In many producers further superheating of the air-steam mixture is done by passing it through an annular space around the lower part of the producer. The cooling effect here is advantageous in checking the formation of clinker.

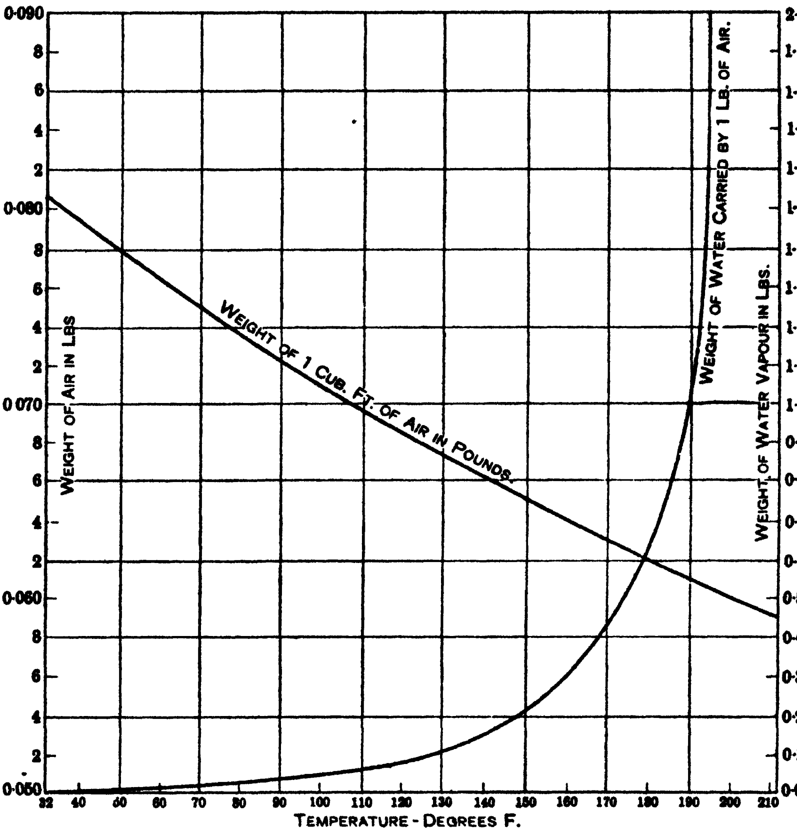


Fig. 57.—Diagram Showing Weight of 1 Cubic Foot of Air at Different Temperatures and Steam Saturation of Air.

Rate of Gasification. A producer must be capable of giving a high rate of gasification with simultaneous production of good gas. Allowing that the necessary temperature is maintained, the quality of the gas will be dependent primarily on intimate contact between the air-steam blast and carbon for equilibrium resulting in the formation of carbon monoxide and hydrogen to be maintained. This will depend on (*a*) the depth of the incandescent zone ; (*b*) the cross-section of the producer ; (*c*) the velocity of the blast. The first condition will depend greatly on the latter factor. The total depth of the fuel will govern largely the volume of the air-steam blast it is possible to admit.

A small fuel depth and a high blast pressure will lead to the whole fuel becoming incandescent, and some carbon dioxide may pass through unchanged. Reduction of the blast to avoid this would lower at once the rate of gasification. On the other hand, excessive depth of fuel offers much resistance to the passage of the blast and the gases, and again, the rate of gasification will be reduced. Deep fuel beds are also conducive to the formation of clinker on the sides of the producer.

If the steam decomposed per pound of coal charged is plotted against the steam supplied in the experiments of Bone and Wheeler, (*J. Iron and Steel Inst.*, 1907, **76**, 126) it is found that the amount of steam decomposed increases as the fuel bed increases in depth. At the optimum rate of 0·4 lb. steam the steam decomposed is as follows:

Depth	3·5 ft.	Steam decomposed	0·19 lb.	or	47	per cent.
„	5·0 „	„ „	0·23	„	60	„
„	7·0 „	„ „	0·36	„	90	„

Since the steam must be decomposed in the primary reduction zone the effect of increase of depth can be due only to the greater extent to which the fuel is pre-heated before it reaches this zone. The depth of the fuel bed also affects the composition of the gas produced. Haslam and Russell (*Fuels and their Combustion*, McGraw Hill, p. 563) show how the equilibrium constant $K = \frac{(CO_2)(H_2)}{(H_2O)(CO)}$ varies for several depths of fuel bed.

Depth ft.	K.
3·50	0·34
4·25	0·40
5·00	0·48
7·00	0·66

The relationship between K and depth is linear and the equation

$$K = 0{\cdot}096L = \frac{(CO_2)(H_2)}{(CO)(H_2O)}$$

can be used to deduce approximately the amount of water in producer gas when its analysis is known. L = depth of fuel bed in feet.

The size and character of the fuel will affect the depth required for the best results. Small or porous fuel, offering large contact surface for the reactions will require less depth than larger and more dense fuel, but the smaller fuel will offer greater resistance to the free passage of the gases. With a fuel having caking tendencies, whereby air channels may form, a greater fuel depth is requisite; again, producers working with bituminous fuel require a depth some 20 per cent. greater than for non-bituminous.

These considerations apply to the *active* fuel depth. A large amount of fuel over that taking part in the reactions may be advantageous in prolonging the time between charging fresh fuel, but beyond that appears disadvantageous. In such upper layers at moderate temperature reversals of the primary reaction are liable to occur, leading to deterioration of the gas, and the mass offers greater resistance to the free passage of the blast, and hence reduces the rate of gasification. In certain producers for bituminous fuels a bell extends downwards from the charging hopper to well below the gas exit pipe. The gases do not pass through this portion, so that the actual fuel depth should be reckoned as from the bottom of the bell. The object of this bell is that the gases from the bituminous fuel may be distilled off slowly and pass through the upper layers of active fuel, where the tarry vapours are supposed to be converted into permanent gases.

In Bone and Wheeler's investigations on a Mond plant, the results of which have been given on page 284, the bell extension was cut off for the second series of experiments, and the active fuel reduced to one-half of that in the first series, namely, from 7 ft. to 3 ft. 6 in., without appreciably affecting the working results. The advantage of the bell is not apparent, and makers appear to be discarding it. Bone and Wheeler's results further show that with proper distribution of the blast through the bed the depth of fuel in many producers is excessive and so disadvantageous, and that the depth seldom need exceed 3 ft. 6 in.; many producers give excellent results with well under 3 ft.

Arrangements for Introduction of the Blast. This is an important question, and the success of a producer is dependent largely upon a proper distribution throughout the fuel bed, otherwise zones of high temperature and the reverse may result.

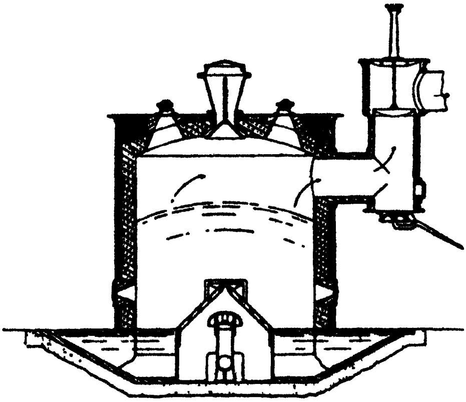


Fig. 58.—Mason Gas Producer.

In producers of larger size, chiefly employed for bituminous coals, the fuel may be supported entirely by a thick bed of ashes, which serves to distribute the air supply from the tuyères. The bottom of the producer extends into a circular pit containing water, which thus forms a seal, yet permits the removal of ash and clinker at any point without interference with the working. The Mason producer, shown in Figure 58, is a good example of this type.

In the Mond producer, the same arrangement of supporting the fuel bed on the ash already formed is adopted, but here, in place of the blast being introduced at the centre, an exterior sloping "grate" attached to the lower sections of the producer extends right round the upper portions of the ash heap. A similar arrangement is illustrated in the Alma producer, Figure 59, designed by Bone and Wheeler.

The distribution of the blast with such a "grate" is good, and large volumes of air can be introduced with very even distribution, giving high rates of gasification and preventing zones of excessively high temperature developing. The clearing of such a grate from clinker, etc., is a more simple matter than with one of the internal pattern, and bars may be renewed at any time, since they are easily accessible.

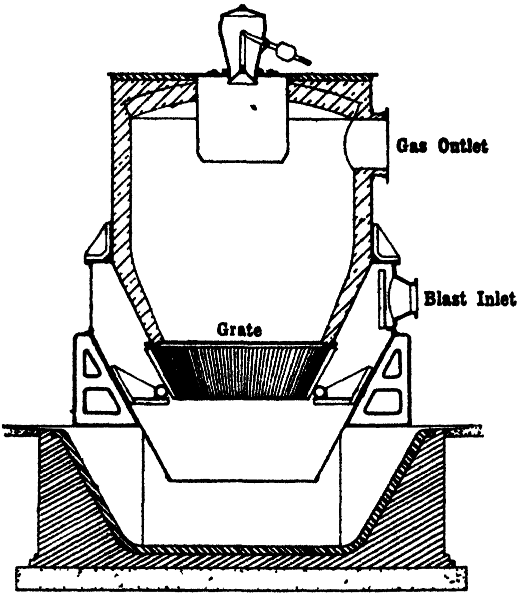


Fig. 59.—Alma Gas Producer.

Small producers usually are fitted with grates which support the fuel bed and are of the closed bottom type, the blast being sent into the ash pit and so up through the grate. Suction producers are almost invariably of the closed bottom type, fitted with a grate. The layer of ash and clinker collecting on the grate serves to protect it from excessive heating, since the zone of intense combustion is thereby raised some inches. In many types the grate is operated mechanically at intervals to permit clearing. Simplicity in action is required in such a case, for at high temperatures something may go wrong, and there is always liability to jamming with a piece of clinker. The area of the grate should be equal to, or but little less than, the cross-section of the body of the producer. Too small an area produces high blast velocity immediately above the grate, developing excessive temperature, which may lead to trouble in operating.

It has already been shown that a large depth of fuel bed is not necessary in a gas producer, and the chief desiderata may be summarized as:

(i) Uniform feed to preserve uniform fuel depth.
(ii) Means of maintaining a loose fuel bed.
(iii) An ash bed of sufficient depth to prevent loss of fuel and heat.
(iv) A uniform distribution of the air-steam blast.

The Kerpely producer (Fig. 60) is a good example of a producer which has been in common use for a number of years and which embodies most of the above.

The fuel is fed from the usual closed type of hopper, and on top of the producer gearing is mounted for operating four bent stirrers of different lengths, which rotate on their own axes, these stirrers being continuously water-cooled. In addition the whole top central portion, including the hopper, rotates slowly, and the fuel is thus broken up continuously during the stages where caking occurs. The firebrick lining does not extend round the hottest zone of the producer; here a space is formed between the inner and outer plates which is cooled by water; this prevents clinker forming and adhering to the sides, as happens so frequently. The revolving "grate" through which the air-steam blast is supplied and the means for automatic removal of the ash may be regarded as salient features in the design.

The grate consists of a single oblong and spherically shaped cone fixed *eccentrically* upon the revolving water trough. The cone is built up of a number of plates, through suitable holes in which the air-steam passes. By the situation of the holes and the rotation of the grate even distribution of the blast takes place, but a very important further control is introduced. In ordinary types of producer, variation in the air-steam pressure is possible only as a whole. In the Kerpely producer the air-steam pressure to the centre portion of the grate can be varied as compared with the exterior portion. In the case of a large producer, should the outer zones reach a higher temperature, with a cooler middle zone, the outer pressure may be reduced and the inner raised until uniform temperature is attained.

The iron water trough carrying the grate is mounted on a ball race and is rotated slowly during working, one revolution in from two and a half to four hours. The eccentric position of the grate and its oblong shape act in crushing down against the lower fixed plates of the producer any lumps of clinker which have formed, so that it passes freely into the rotating trough, where by means of a scraper it is discharged automatically.

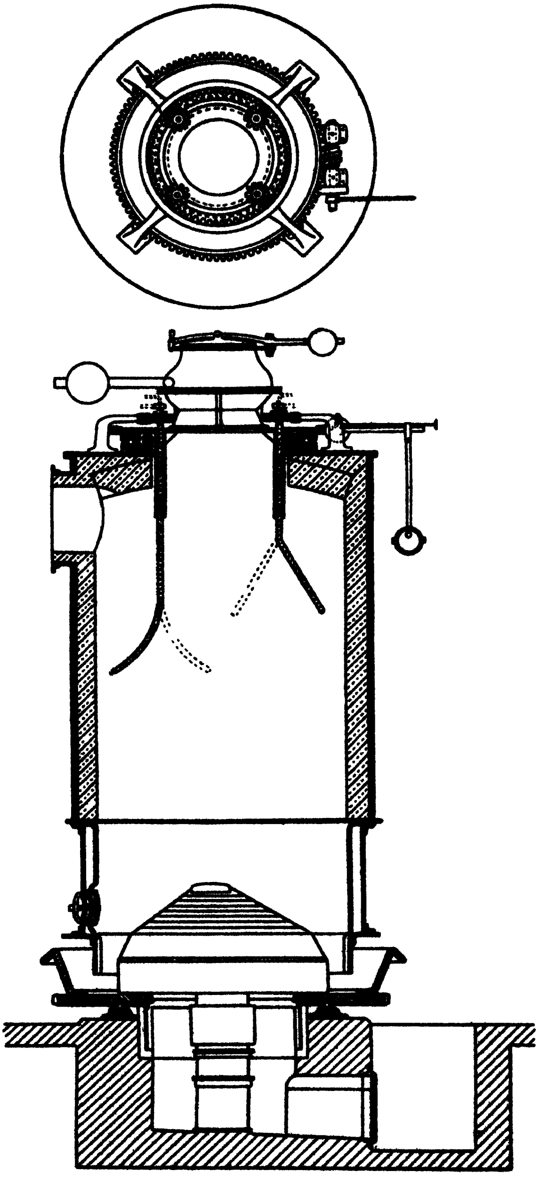


FIG. 60.—Sectional Diagram of Kerpely Producer.

The Cleaning of Producer Gas. For use in engines producer gas must be delivered cool and free from anything other than traces of dust or tar. For use as a fuel such efficient cleaning is not normally necessary although trouble with sticky or choked valves may sometimes result. The plant necessary depends also upon whether the fuel used is coal, coke or anthracite. For the latter a simple coke scrubber into which water is sprayed is normally sufficient. Coke may give as much as 1 per cent. of tar and it is not safe to assume that a tar remover can be dispensed with for engine purposes. The most common type of scrubber is the water-washed coke tower. This is followed by a tar extractor, of which there are many forms. A common form is a chamber containing a number of baffle plates against which the gas impinges with change of direction and a final filter chamber containing sawdust. A second form comprises a chamber in which a wire brush rotor revolves at high speed in the gas to beat out the droplets of tar.

The tar recovered from gas-producer plant can be gasified in certain types of producer where the vapours distilling from the upper layers of the hot fuel bed are carried downwards through the upper part of the fuel bed. Such arrangements are normally confined to small producers.

Most of the producer gas made to-day is used for direct furnace work. In this case the gas is fed direct without cooling to the combustion flues and no attempt at cleaning is made. Where one producer serves a number of furnaces the gas may be scrubbed hot by sand or coke to remove dust which might otherwise give trouble with valve operation.

The Efficiency of Gas Producers. A practical difficulty in measuring the efficiency of a gas producer is the measurement of the large volume of hot gas. The pioneer work of Sir R. Threlfall (*J.S.C.I.*, 1907, 355) greatly helped towards a solution of this, but normally the result is arrived at via the carbon balance.

The following example will make the method clear.

Coal (brown) employed—contained 57·7 per cent. carbon.

Composition of the gases:

Carbon dioxide	2·8
Carbon monoxide	30·5
Methane	2·0
Calorific value. B.Th.U.	159

Hydrogen, nitrogen, etc., need not be considered, but only those constituents containing carbon.

The volumes first are converted into weight by multiplying by the weight of 1 cu. ft. of each gas in lb. (see Table I., Appendix):

	Volume in cu. ft.		Weight of 1 cu. ft. in lb.		Weight in cu. ft. (lb.).
Carbon dioxide	2·8	×	0·1226	=	0·3433
Carbon monoxide	30·5	×	0·0780	=	2·3790
Methane	2·0	×	0·0447	=	0·0894

From the composition of these gases, 44 lb. carbon dioxide contain 12 lb. carbon; 28 lb. carbon monoxide contain 12 lb. carbon; and 16 lb. methane contain 12 lb. carbon; then:

	Lb. of carbon in gas.
Carbon dioxide	$0{\cdot}3433 \times \frac{12}{44} = 0{\cdot}0936$
Carbon monoxide	$2{\cdot}3790 \times \frac{12}{28} = 1{\cdot}0196$
Methane	$0{\cdot}0894 \times \frac{12}{16} = 0{\cdot}0670$
Total weight of carbon in 100 cu. ft. gases	1·1802 lb.

As 1 lb. of fuel charged contains 0·577 lb. of carbon,

Yield of gas per lb. of fuel $= \dfrac{0{\cdot}577 \times 100}{1{\cdot}1802} = 48{\cdot}9$ cu. ft., and per ton $48{\cdot}9 \times 2240 = 109{,}500$ cu. ft.

The *efficiency* of a gas-producer plant is the ratio of the heat units in the gas to those in the fuel charged.

The *cold gas* efficiency is obtained from the calorific value and volume at 0° C. and 760 mm. In the *hot gas* efficiency it would be necessary to add to this value the sensible heat of the gases as delivered to the furnace, reheaters, etc., deducing this from their weight and mean specific heat. In the case considered above the cold gas efficiency would be:

Calorific value of gas (net) per lb. of fuel $= 48{\cdot}9 \times 159 = 7775$ B.Th.U.
" " 1 lb. of fuel = 9720 B.Th.U.
Efficiency $= \frac{7775}{9720} \times 100 = 80$ per cent.

Bone claims that the *net* calorific value of the gas should be taken, and that the coal required for raising any steam for the blast and for operating the blower, together with fuel required equivalent to the mechanical work of washing the gas, should be included, that is, an over-all efficiency.

The approximate rating in B.H.P. of a producer plant is given by:

B.H.P. = tons gasified in 24 hours × 100.

When producer gas is used as a fuel for gas engines it is interesting to note that the air/gas mixture entering the engine has a higher calorific value than the corresponding mixture of air and coal gas.

PRODUCER-GAS PLANTS

The choice of gas-producer plant for any particular purpose will depend upon the nature of the gas required and upon whether it must be clean. The size of the installation will also decide whether the operation shall be by hand or mechanical. It is sufficient for the purposes of this book to illustrate one or two types of modern plant and to draw attention to the devices used for feeding, poking, ash removal, etc.

Suction-Gas Producers. The general arrangement of a typical suction-gas plant for power purposes is shown in Figure 61. The producer B is fed with fuel from the hopper A, which must be provided with some feeding device so that the fuel may be dropped into the "container" below without the admission of air. A rotary type of feed-hopper, Fig. 62, is employed in the Crossley plants. The container must have a sufficient fuel capacity to enable it to supply the producer for about two hours, in order to avoid the necessity for frequent charging.

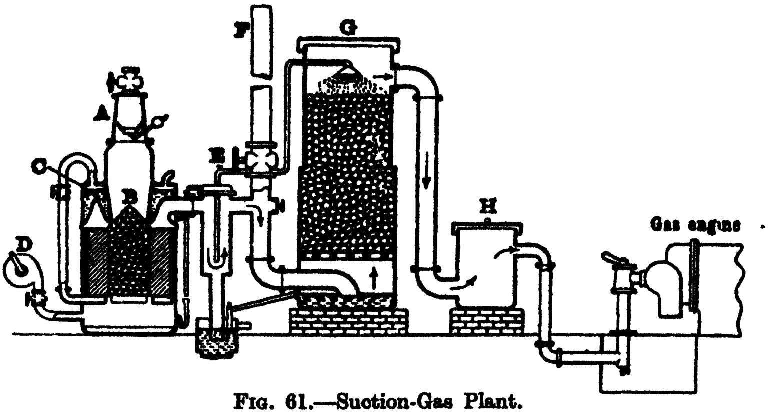


Fig. 61.—Suction-Gas Plant.

Around the top of the producer the vaporizer C is situated; in this case it is of the boiler type. The air inlet is shown at the top right hand, and the steam-saturated air passes down through a pipe, with a valve, to the closed bottom of the producer. The fan for starting is shown at D. The hot gas leaving the producer passes through

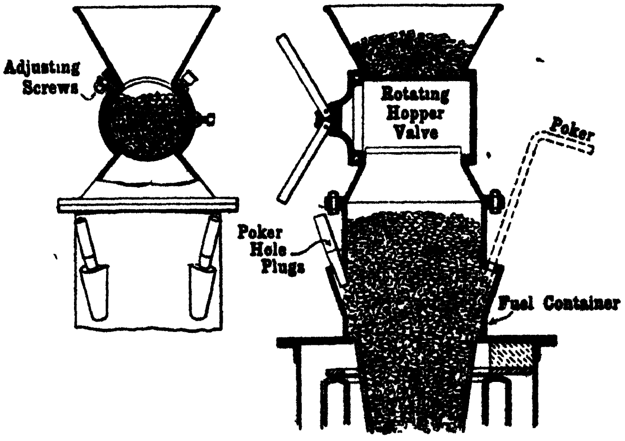


Fig. 62.—Crossley Rotary Feed-Hopper.

a vertical separator E; in some plants this is jacketed and the ingoing air thus pre-heated. Here dust is deposited, and some tar condensed, which passes down into the water seal at the bottom.

The gas leaving the separator enters a vertical pipe, which extends upwards to the open air through F. When starting up the valve E is opened, so that all poorer gas may be sent to waste until a sufficiently good quality is obtained, as found by its burning at a suitably situated test cock. When running E is closed, the gas passing through a water seal into the coke scrubber G. This provides all the scrubbing required when anthracite is the fuel, but when coke is employed an additional scrubber must be provided.

From the coke or sawdust scrubber the gas passes into the expansion box H, from which the piston draws the supply for the next charge into the cylinder. Generally it is regarded as desirable for the volume of the expansion box to be at least three-quarters that of the cylinder charge. The expansion box provides a supply of good gas ready to fill the cylinder in the short space of time occupied by the suction stroke, which would not be the case had it to draw directly on the pipes, coke scrubber, etc. It tends to minimize the fluctuations in flow of the gas through the whole system which must occur between successive charging strokes.

In order to determine when good gas is coming through, a test cock is placed as near the engine as is convenient, generally on the expansion box, and a further waste pipe is installed here in order that the poorer gas from the scrubbers and various connections may be swept out.

Suction Gas from Bituminous Fuels. Two types of plant are used (1) in which the tar is destroyed and (2) in which the tar is condensed and removed from the system. The principle of type (1) is the causing of the distillation products to pass through part of the fuel bed. The Dowson plant is selected to illustrate this principle; a diagrammatic view is shown in Figure 63.

The producer is so constructed that the gases are withdrawn about half-way up the fuel bed. The air-steam supply passes into the water-sealed bottom of the producer, this water-seal permitting the withdrawal of clinker and ash during working, and a controlled secondary air supply is admitted at the top of the producer. The suction is obtained by a fan placed after the sawdust scrubber. The heat resulting from the actions in the lower sections of the fuel slowly distils out the volatile constituents of the raw fuel lying in the upper sections, and these are drawn down with air for their combustion through a zone at high temperature on a level with and a little above the gas exit. The coked fuel thus gradually works downwards to the section where the producer gas reactions proper take place.

The hot gases pass through a vaporizer where they are cooled, at the same time raising the necessary steam for the plant. Afterwards they pass through suitable scrubbers and finally a sawdust scrubber. Where there are several engines, or gas has to be supplied for heating purposes also, a gasholder is provided. This is unnecessary with only one engine, the gas production being regulated by a suitable governor. It is claimed that with ordinary bituminous coal, lignite and some other fuels, the tar is removed completely in the producer, and no mechanical or other tar extractor is required.

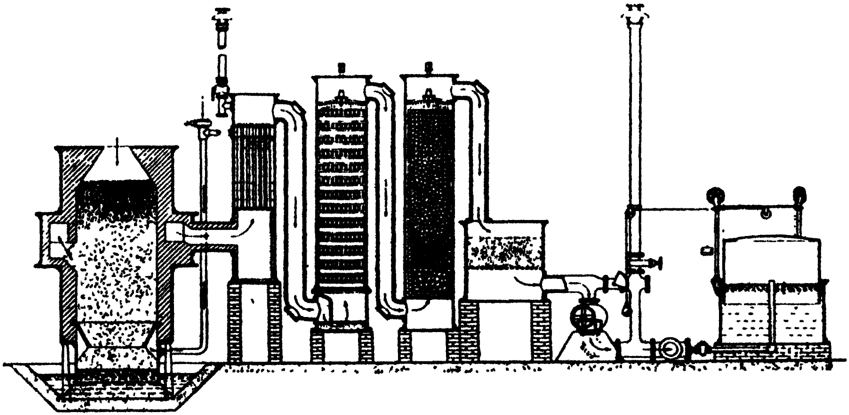


FIG. 63.—Dowson Bituminous Coal Suction Plant.

The gas composition from such a plant is approximately CO_2 7·2, CO 23·9, H_2 16·0, CH_4 1·0, N_2 51·9.

Suction Producers for Furnace Heating. In certain cases where gas producers are used for furnace heating these are of the suction type, the suction being supplied by the chimney of the setting. Owing to the low pressure of the draught such producers have a relatively large grate area and are built into the brickwork of the furnace in order to reduce the loss of heat by radiation, etc., and to supply the gas as hot as possible to the combustion flues or chamber.

Figure 64 illustrates such a producer diagrammatically. The fuel is fed into a vertical shaft A and the bed is supported partly on the step grate B and partly on the bottom brickwork. The firebars of the grate are flat castings about 9 in. wide; they are spaced about 7 in. apart and generally slope inwards at a small angle (8°). The pull of the chimney, acting through the flue C, draws air through the spaces between the firebars so that the oxidation zone lies between B and C, BC′ being the fuel bed proper and about 4 ft. to 4 ft. 6 in. in thickness. Steam is supplied by projecting a fine spray of water against the grate, from a nozzle placed in a suitable position. The chamber below the grate is normally closed by a door E with air ports in it in order to keep up a reasonable temperature for the vaporization of the water spray, and is opened only when it is necessary to rake out ashes from below the grate. The bottoms of such producers are normally wet owing to the collecting of water which is not evaporated. The work done by a producer of this type is limited by the pull of the chimney; where this is more than adequate the air supply is limited by moving the louvres in the door. A most important precaution which must be observed is that the level of the fuel bed must not approach the arch F or, when the upper door is opened for charging, air may be drawn into the hot gas flue when an explosion would result.

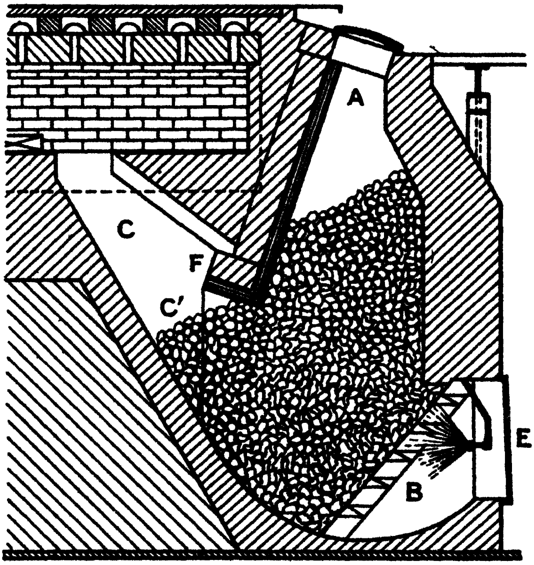


FIG. 64.—Diagram of a Step-Grate Producer.

A producer of the size shown in Figure 64, i.e. shaft 4 ft. × 4 ft., grate area 14 sq. ft. and fuel bed of 4 ft. will gasify coke at the rate of 2 cwt. per hour with a chimney pull of one-fifth of an inch of water. This is equivalent to a rate of gasification of 16 lb. of coke per sq. ft. of grate area per hour.

The control of a producer of this type is simple, the air supply being checked by analysis of the gas and the rate of feed of water to the vaporizing nozzle being controlled in terms of the weight of fuel gasified. The output of the producer is, of course, controlled by the suction or pull of the chimney. In the example above about half of the pull is required to induce the secondary air for combustion so that the pressure difference in the producer is only $\frac{1}{10}$th in. Increase of this pressure difference will, of course, increase output. A producer of this type can be operated as a pressure producer by closing the outer door and supplying the air-steam blast under pressure.

Pressure Producers. There are many forms of gas producer in which the air and steam are supplied under pressure, but most of these are variations of only a few types. It will be sufficient to describe in detail one or two typical producers of modern design. Proprietary producers will generally conform to one of these types.

Pressure producers are used principally for the production of gas for furnace heating and are therefore built in close proximity to the furnace so that the sensible heat of the hot gases can be utilized in the furnace. In addition the tar vapours are allowed to remain in the gas and enhance its calorific value. It is estimated that the increase due to tar vapour may be 15–20 B.Th.U. per cu. ft. Cleaning of the gas is, therefore, not normally attempted although in special cases dust filters (e.g. sand towers) are used which can be maintained at a high temperature.

In pressure producers the pressure is produced either by steam injectors or by steam-driven turbo-blowers. The latter are to be preferred in that they are positive in their action and are susceptible of easy control to meet the requirements of varying load. An injector system is not satisfactory in that the amount of air injected cannot be altered without also changing the air-steam ratio, which is undesirable. Load variations can only be met by altering the steam nozzles, an inconvenience in normal working.

Morgan Producer. The Morgan producer may be taken as an example of the common type of mechanical producer of suitable size (1500–3000 lb. coal per hour) which is used as an adjunct to furnace operations in metallurgical work generally. The Kerpely producer, Figure 60, is also in very common use. Producers of this type which burn coal frequently have stirring arms or mechanical pokers and levelling devices with which the surface of the coal is agitated to avoid caking and channelling.

The poker may take the form of a water-cooled oscillating finger (Wellman), water-cooled stirring arms (Wood), rakes with water-cooled prongs (Chapman) or some similar device. The Morgan producer has no poker but a levelling device. A diagrammatic view of the producer is shown in Figure 65. The body of the producer and the ash pan rotate round a central pillar carrying blast inlets and a spiral scraper bar which pushes the ash towards the outside where it is removed by an intermittently operated plough. The blast inlets are from three hollow radial arms and also from a hollow ring or mantle running round the producer. This arrangement ensures even distribution of the blast over the whole fuel bed. The producer body, 8 ft. high by about 11 ft. diameter, is brick-lined with a water jacket to cool the brickwork sufficiently to prevent slagging with the coal ash. The water jacket accommodates the seal plates of the cover and top casting. The coal is fed continuously by an automatic feed operated by the rotation of the producer. It is claimed that this producer will gasify up to 3000 lb. of coal per hour or about 35 lb. per sq. ft. of grate area per hour. The gas has the composition CO_2 3·5, CnHm 0·9, CO 29·0, H_2 12·0, CH_4 2·6, N_2 52·0 at 180 B.Th.U. per cu. ft. The steam consumption to produce this gas is about 0·17 lb. per lb. of coal.

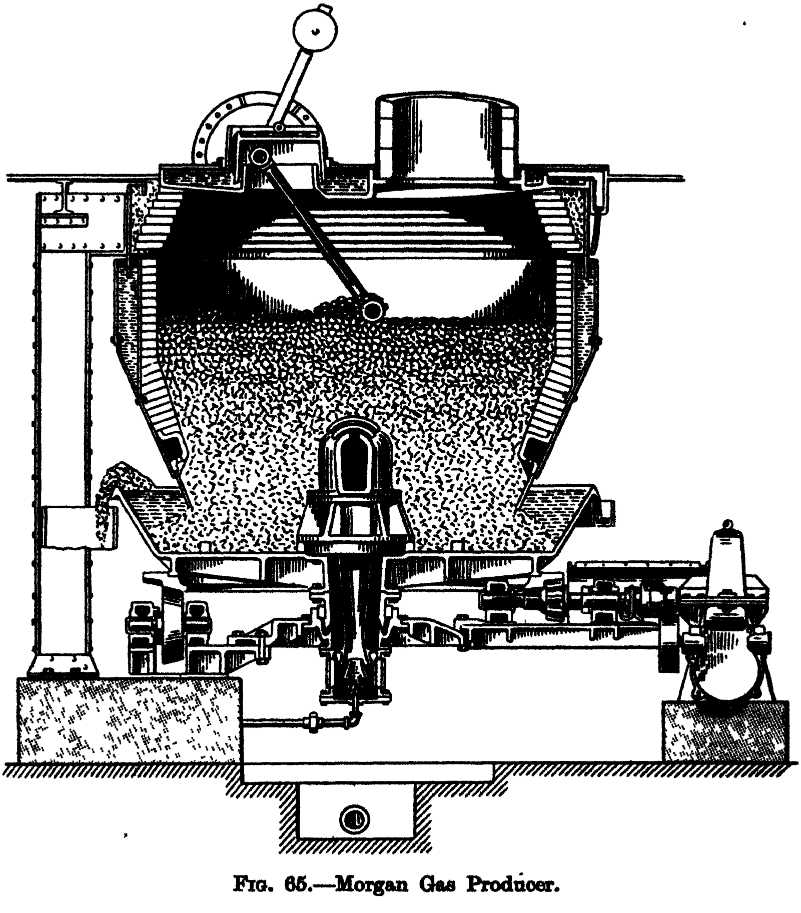


FIG. 65.—Morgan Gas Producer.

Mond Producer. The Mond producer is typical of the large stationary producer capable of supplying large volumes of gas through pipe lines for power or heating purposes. This producer originated in 1883–5 for the production of gas with the simultaneous recovery of ammonium sulphate. In order to increase the yield of ammonia very heavy steaming was resorted to, amounting to about 2 lb.

steam per lb. of fuel. Yields up to 90 lb. of sulphate of ammonia are reported with 150,000 cu. ft. of gas per ton of coal, the gas having a calorific value of 150 B.Th.U. and containing 1·6 per cent. of nitrogen.

The producer is a vertical one but with a very deep fuel bed. The hot gas leaving the top at over 500° C. passes through a heat exchanger which pre-heats the air to about 250° C. The pre-heated air is further pre-heated, with the steam for the blast, in an annular space round the producer and enters the fuel bed through spaces in the grate, which takes the form of an inverted truncated cone.

Owing to the large excess of steam used the reactions are influenced in the direction of CO_2 and the calorific value of the average gas is low. A typical Mond gas is CO_2 18·0, CO 10·0, H_2 25, CH_4 3·0, N_2 44, 145 B.Th.U. per cu. ft.

Since the introduction of synthetic ammonia manufacture the use of Mond plants has gradually decreased. To-day ammonia recovery is largely abandoned and the plants in use are operated with less steam more after the practice of non-recovery producers.

Koppers Producer. This producer is an example of the large vertical producer, with complete mechanical operation, which is used for the manufacture of producer gas for distribution to furnaces. The producer is shown diagrammatically in Figure 66. The generator itself is really an annular vertical steam boiler of 5 to 10 ft. internal diameter. The upper portion, carrying the gas offtakes RR′, is brick-lined. The grate H, a truncated cone with air-spaces, is rotated slowly by a driving mechanism which is also linked FF′ to the feed-hopper E. This rotation of the grate brings the ash down into the ash pan, which rotates with the grate, from which it is scraped out at one point by a plough arm. The plate carrying the feed-hopper rotates on roller bearings and leakage of gas is prevented by the water-seal Q. The fuel is contained in the hopper E and, when the feed mechanism is operated at each revolution of the grate the bell S is lowered and the fuel introduced via the special distributing extensions GG′ which give a level surface to the fuel bed. The amount fed has, of course, to be regulated in terms of the ash removed so as to maintain a uniform depth of fuel bed at a determined distance clear of the rotating distributors. Poke holes are arranged in the producer top to allow of poking of the bed and to give measurements for adjustments to the feed mechanism.

The water space of the producer casing is connected to the steam collector L situated above the service platform of the producer. The water level is half-way in the steam collector so that circulation takes place between this vessel and the producer jacket. The steam produced, at from 7 to 70 lb. pressure, is more than sufficient for the pro-

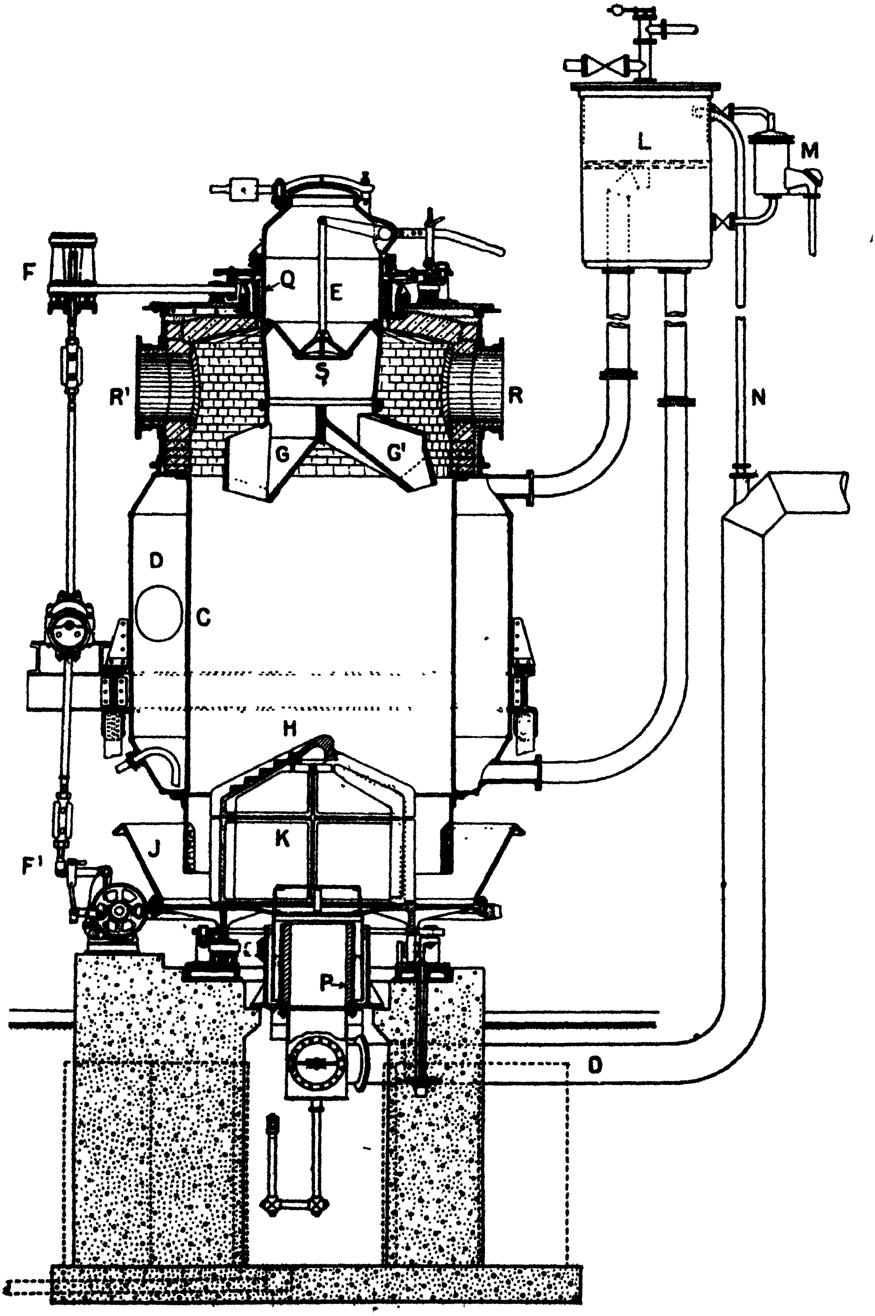


FIG. 86.—Koppers Gas Producer.

ducer. The whole procedure ensures sufficient cooling of the generator casing without the risk of corrosion on the inner surface which can be the result of using cold cooling water.

The steam to the generator is supplied via the pipe N to the air supply pipe O. The steam-air blast passes to the wider side of the grate, leakage being prevented by the water seal P, and is distributed uniformly by the openings between the leaves of the grate.

It is claimed that this producer will also operate satisfactorily with fuels of small particle size.

Slagging-ash Producers. In order to overcome the difficulties of dealing with fuels which give trouble through clinker formation several types of producer have been evolved in which the temperature of operation is raised to such a height that the ash melts and the molten material can conveniently be tapped from below the grate. In such producers the high temperature is reached by blowing with air only and very high rates of gasification are achieved. The tuyères are water-cooled and the brickwork in their neighbourhood is cooled, by having a water pipe embedded in it, in order to prevent fluxing with the ash. Steam may be introduced above the fluxing zone. The Würth producer is perhaps the best known although, generally speaking, slagging-ash producers are not common. The producer is rather similar to a small blast furnace, the air being supplied under pressure through several water-cooled tuyères. The fuel bed is thick to allow of good pre-heating and the charge is mixed with limestone (perhaps 10–15 per cent.) or other material to help flux the fuel ash. The sensible heat of the gases is used to pre-heat the air and increase the working temperature.

One advantage of producers of this type is the small space occupied. A disadvantage is the heavy cost of maintenance of the linings.

The Use of Oxygen in Producer Practice. Attempts have been made to reduce the normal high nitrogen content of producer gas by enriching the air supply with oxygen. Until sufficiently cheap oxygen becomes available industrially the attempts have only theoretical interest, but Jeffries (New Engl. Gas Assoc., 1921) has calculated that it should be possible to produce with oxygen a gas of 383 B.Th.U. and containing 28 per cent. H_2 and 58 per cent. CO. An oxygen producer could be operated either as a slagging producer or as a continuous water-gas plant. The proposal would seem to hold most promise as a process in which the blast is enriched with oxygen, steam being added to keep the temperature under control. By this means the output in terms of cu. ft. of gas per sq. ft. of grate area would be considerably increased and the calorific value of the gas would be higher.

It can be shown that the following increases of calorific value are possible:

O_2 in air.	H_2 per cent.	CO per cent.	CO_2 per cent.	B.Th.U. per cu. ft.	
				Coke.	Coal.
21	7	30	5–7	118	155
40	14	39	5–7	170	250
60	19	57	5–7	245	320
80	22	63	5–7	270	340

If commercial oxygen should become available at a sufficiently low cost it would seem that development would take place by the use of slagging-ash producers since the temperature in the oxidation zone will certainly be high.

Utilization of Coke Breeze. The difficulties of dealing with slacks or fuels of small size have been referred to. Certain of the modern producers claim to be able to deal with such material satisfactorily, but it is certain that much more attention must be given to the operation of the producer. Experience at the Fuel Research Station (*Ann. Rep. of Director of Fuel Research*, 1932, Appendix) has shown that up- and down-running, after the fashion of water-gas manufacture forms a satisfactory solution. Using a Humphreys and Glasgow water-gas generator alternate ten minutes up- and down-runs were satisfactory for gas-retort breeze (on ½ in. 24, ½—¼ in. 22; ¼—⅛ in. 24; ⅛—0 in. 30 per cent.). The fuel bed was 4 ft. thick, charging was necessary every two and a half hours and clinkering every twenty-four hours. With fine fuels a thin fuel bed is best since the pressure drop across the bed should not be more than 9 in. (water gauge).

The following are data from the gasification of breeze containing 7·8 per cent. moisture and 11·9 per cent. ash and using 0·77 lb. steam per lb. of breeze.

Coke charged per hour	254 lb.
Consumed per sq. ft. grate area per hour	16·0 lb.
Gas made per ton	145,960 cu. ft. 160·6 therms
Efficiency	62·4 per cent.
Gas calorific value	110 B.Th.U.
C lost in clinker and ash . . .	5 per cent. of coke charged

The analysis of the gas was CO_2, 10; CO, 21; H_2, 13·0; N_2, 56·0 per cent.

Producer Gas for Motor Transport. The design of a small gas producer for road transport was attempted as long ago as 1819 and an investigation of the possibilities was made by a Government Committee in 1919 which embraced road trials. Since then commercial exploitation has produced a number of satisfactory producers for use particularly with tractors, in districts where petrol is expensive, e.g. the colonies. In France even greater attention has been given to the development of gas-driven vehicles; periodic organized competitions and "rallyées" have been held since 1920.

The fuel which holds most promise for this purpose is charcoal and development will probably continue in places where wood is plentiful. Charcoal as prepared is light and friable and briquetting is resorted to in order to reduce bulk and increase the output of the producer. Generally speaking, any smokeless fuel of good combustibility is suitable for this purpose; other fuels are less suitable owing to the difficulty of clearing the gas thoroughly. The difficulty is overcome in certain types of producers, employing down draught, in which volatile tarry products are consumed in the fuel bed. The modern producer has certain essential features such as light construction, good insulation, down or side draught, water-cooled tuyères and a convenient shape so that it fits on to the running board of the car or other suitable position. The weight (2½ cwt.) and awkward shape of producers and the bulkiness of the fuel used in them are the chief drawbacks to this type of power, the extra load carried reducing efficiency and the fuel reducing cargo space. The ten to twelve minutes required for starting up in the morning is another drawback.

Many trials of producer-driven vehicles have been made and it has been deduced that it is cheaper to use petrol than charcoal provided the petrol cost is less than 25 per cent. of the running costs of the vehicle, even if the cost of the producer fuel were nil. In certain colonies, where labour is cheap and petrol expensive, this conclusion is evidently in favour of the producer. As regards efficiency, given the same engine, power output with producer gas is only 60–70 per cent. of that developed with petrol. This loss of output can be largely prevented by increasing the compression ratio or improving the induction system to give greater freedom of movement of the gas.

The Imperial Institute (*Bull.*, 1931, 29, 437) quote charcoal requirements for a one-ton truck as 1·3 to 1·5 lb. per ton mile (C.V. charcoal about 7420 B.Th.U.).

The Koela is perhaps the best-known British producer. It is manufactured in three sizes to suit light, 60 and 80 B.H.P. vehicles. The compression ratios of the engines vary from 6¼ to 7 : 1 and starting up takes from five to ten minutes. The coke consumption for a 30-cwt. lorry is stated (*Comm. Motor*, 1934, 629) to be 84 lb. per 100 miles.

Russell (World Petroleum Congress, 1933) quotes for a ninety-four-mile journey 102 lb. of charcoal in comparison with 7 gallons of petrol.

Since the total load was 3 tons the consumptions per ton mile are charcoal 0·36 lb. and petrol 0·025 gallon.

BLAST-FURNACE GAS

This secondary product of the production of pig iron in the blast furnace is a fuel of great importance not only for furnace use in iron and steel production, but also as a source of heat energy for electricity production.

The quantity of heat energy available as blast-furnace gas is considerable. The production of pig iron in Great Britain prior to the war was about 9–10 million tons per annum. Post-war this has been reduced to a figure, when the industry is working to reasonable capacity, of between 7 and 8 million tons. In the years preceding the war, whilst coke was the principal fuel, an appreciable amount of raw coal was also used, particularly in the Scottish producing area, where splint coal was available. In 1920, for example, 8,034,717 tons of pig iron were made, requiring 10,036,210 tons of coke and 2,062,360 tons of raw coal. During recent years, however, the utilization of raw coal has almost ceased, and within the last few years has amounted to less than 100,000 tons per annum.

For practical purposes, it is only necessary to consider blast-furnace gas from coke-fired furnaces. The composition of this gas will vary with the quantity of coke used for smelting; the higher the coke composition, the higher the calorific value of the gas. Coke consumption has been considerably reduced during recent years. The equivalent quantity of *coal* has been reduced since 1913 from 41·4 to 35·7 cwt. per ton of pig iron produced. The actual consumption of coke varies considerably in the different districts in Great Britain, from 19 to 25 cwt. per ton of pig iron. Approximate figures for coke consumption and volume and nature of gas produced are given in Table LIV.

TABLE LIV

PRODUCTION OF BLAST-FURNACE GAS IN GREAT BRITAIN

	Lincs. S. Yrks.	North-ants.	North-East Coast.			S. Wales.	W. Coast.	Scotland.
Grade of iron .	Basic	Foundry	Foundry	Basic	Hematite	Basic	Hematite	Basic
Coke consumption cwts. per ton pig . .	25	26	23	20	21	18	19	19
Equivalent coal consumption.	37·5	39	34·5	30	31·5	27	28·5	28·5
Gas analysis:								
CO_2 . . .	9·0	9·0	9·0	11·5	12·0	9·5	10·0	9·0
CO . . .	29·0	30·0	30·0	28·0	27·0	27·5	27·5	29·0
$CH_4 + H_2$ . .	3·5	3·0	2·0	2·0	2·0	4·0	2·5	—
N_2	58·5	58·0	59·0	58·5	59·0	59·0	60·0	62·0
C.V.–B.Th.U. per cu. ft. . .	112	114	111	104	100	109	104	100
Vol. per ton pig —cu. ft. . .	198,000	203,000	178,000	158,000	188,000	145,000	149,000	126,000

Utilization of Blast-Furnace Gas. About 60 per cent. of the calorific value of the coke charged to a blast furnace is returned in the form of gas. Of this, in a modern plant equipped with modern stoves and blowing engines, about 40 per cent. is used to meet the heat and power requirements of the blast furnace itself, 25 per cent. of the gas being required for heating the stoves, 15 per cent. to produce the power required for the blowing engines and the auxiliary plant; and the remainder would be available for heat and power production for the steelworks or plant other than the blast furnaces.

The surplus gas can be used either directly for power production in gas engines, or indirectly for generating steam for turbo-alternators. Generally speaking, the capital and maintenance costs of the gas engine are higher, but it has the advantage of a higher thermal efficiency, about 33 per cent. With the advances in modern steam generation, practically the same efficiency can now be obtained in power station practice, but is not obtainable with the size of unit normally installed in iron and steelworks power houses. Should future developments justify the installation of turbine sets as large as 12,000 kw., their efficiency might become high enough to compare favourably with the gas engine, as the following figures, given by Webber, reveal:

Steam Turbine (12,000 *kw.*):	
Boiler efficiency	0·87
Turbine efficiency	0·322
Overall efficiency	0·251
Heat consumption	13,600 B.Th.U./kWh.
Gas Engine (7,000 *kw.*):	
Overall efficiency	0·290
Heat consumption	11,770 B.Th.U./kWh.

At the moment, however, the gas engine is still the more efficient method of producing power from blast-furnace gas, especially where blowing power is concerned, since the size of unit is restricted necessarily by the demand of the furnace concerned.

Where efficiency is of less importance, i.e. when the whole of the gas cannot be utilized, the steam-turbine generating plant has definite application. In addition, where there are possibilities of gas shortage, the steam unit can still be operated by burning oil or solid fuel, whereas the gas engine may have no alternative fuel.

Blast-Furnace Gas as a Fuel for Metallurgical Furnaces. The temperatures required in metallurgical furnace practice are generally too high to allow of blast-furnace gas, with its low calorific value, being used without regeneration; in most cases both gas and air regeneration is required. Even then, the temperature is insufficient for certain metallurgical processes such as the open-hearth process, where working temperatures in certain parts of the furnace may exceed 1800° C. In such cases the blast-furnace gas may be enriched by the addition of coke-oven gas, a suitable proportion being two volumes of blast-furnace gas mixed with one volume of coke-oven gas, giving a calorific value of the mixture of about 230–250 B.Th.U. per cu. ft. This system has the great advantage that the calorific value of the mixed gas can be adjusted from time to time to suit conditions of furnace operation, e.g. a richer mixture can be used for fast melting down of the scrap. In some cases, tar or liquid fuel is also added in order to give a reducing character to the flame.

For re-heating purposes, however, where temperatures do not exceed 1200 to 1300° C., gas is an excellent fuel provided air and gas regeneration is employed.

Heating costs are, as a rule, considerably lower than with alternative fuels. The limitations of metallurgical furnace practice such as the charging and withdrawal of stock, high radiation and external cooling loss, high temperatures of the exit gas make it impossible to attain the high heat transfer efficiencies that are possible in boiler practice, but even then blast-furnace gas is cheaper than alternative fuels, and with efficient combustion control and operation of the furnace to capacity, good results can be obtained.

In order to utilize the gas to maximum efficiency, it is important that the pressure of the gas should be uniform, that combustion control should be efficient, that the gas should be clean, and that the amount used for each purpose should be carefully measured.

Uniformity of gas pressure is a factor of the greatest importance. Since the blast furnace operates under rather varying conditions, some method of control of pressure must be adopted. The most effective method is the use of a gasholder, which serves both for storing the gas and for distributing it. Since the volume of gas produced is very large, storage is possible only with the gas produced during short periods, so that the gasholder acts more as a governor than as a storage vessel. Even so, in recent years holders have been installed of capacities up to 10 million cu. ft.

Failing a gasholder, which is necessarily an expensive installation, many works have adopted a system of automatic pressure control, so that gas is delivered to the various units at a predetermined pressure. If the supply of gas falls, the least important units are cut off automatically, so as to allow of pressure to other units being maintained; suitable methods of signalling being adopted to warn the operators of the plants affected.

With gas available at constant pressure, the correct proportioning of gas and air to a consuming unit becomes a comparatively easy matter. This is particularly the case where suitable burners are used and a number of burner designs now available allow of almost theoretical proportioning of gas and air with a consequent resulting combustion efficiency. Such burners are particularly useful in boiler and stove practice, where high heat transfer efficiency can be obtained.

In metallurgical furnaces, where regenerators are used, there are limitations of furnace design and practice which do not allow in all cases of suitable burners being used. In such cases the correct proportioning of gas and air is obtained by suitable port and furnace design, and by chemical control.

Apart from customary chemical methods to control the composition of the exit gases, measurement is probably the most effective method of controlling gas supply to ensure efficiency in use.

The gas leaving the blast furnace has a high dust content, the proportion of which varies with the operation of the furnace. Most of the dust is deposited in flues and dust-catchers, but further cleaning is necessary if the gas is to be used efficiently, the final degree of cleanliness being 0·2 grain per cu. ft. for stoves, boilers or metallurgical furnaces, and about 0·005 grain per cu. ft. for gas engines. The modern trend is in the direction of complete cleaning of the whole of the gas, and both wet and dry methods are used. Wet methods depend in particular upon the attainment of intimate contact between gas and water, either in towers or by fan disintegrators of the Theisen type. Dry methods include filtration through bags (Halberg-Beth system) or electrostatic precipitation (Lodge-Cottrell system). Choice of method depends on factors such as degree of cleanliness required, quantity of water available and its cost, and the cost of power. The following are typical gas cleaning results given by Harbord (*J. Iron and Steel Institute*, 1928, **117**, 235).

System.	Scrubber and Thiessen Disintegrator.	Lodge-Cottrell plate type.	Halberg-Beth.
Gas cleaned per hr., million cu. ft. .	over 5	over 3	2
Dust in crude gas, gm. per M^3 .	2–3	4–6	3–4
Dust in clean gas	0·03	0·3 [1]	0·025[2]
Electric power, units per 1000 cu. ft.	0·22	0·022	0·08
Water, gals. per 1000 cu. ft. . .	6·0	—	v.s.
Costs, pence per 1000 cu. ft. . .	0·115	0·027	0·066

[1] 0·004 after final spray for engines.

[2] Recent developments now indicate a much higher efficiency of dust removal.

Before the days of efficient gas cleaning the measurement of volume was a difficult matter. These difficulties have now been overcome by cleaning, and measuring is almost universally carried out in composite works where the blast furnace gas is required as a steelworks fuel. As a rule, measurement is made by orifice-plate meters.

Reference Books

Modern Gas Producers, by N. E. Rambush. (1923.) Benn Bros.
American Producer Gas Practice, by N. Latta. (1910.) D. Van Nostrand.

PART IV

FUEL ANALYSIS, CALORIMETRY AND CONTROL OF FUEL SUPPLY

CHAPTER XVII

FUEL ANALYSIS

Space does not permit of lengthy treatment of methods of sampling and analysis and neither is this necessary since the long-felt need for the adoption of standard methods has been met by the publications of the Fuel Research Board (1923) and the British Standards Institution methods on the sampling and analysis of coal,[1] both for the home market and export, and by the Institution of Petroleum Technologists methods for petroleum products, which are included, as required, in B.S.I. specifications for these.

Such standard methods should be followed in detail, but some brief outline of the more important and reference to alternative methods will be given.

Before any analytical process is carried out it is most essential that the material examined shall be, as far as it is possible, truly representative of the bulk ; in other words, shall be a representative sample. With homogeneous liquid and gaseous fuels this is reasonably easy to ensure, but with solid fuels, especially with material of very varying size, this is not easy to attain, and the procedure laid down in the B.S.I. publications should be carefully followed or disputes on results will inevitably follow. With the increasing adoption of purchase of fuel on a basis of composition and calorific value the importance of good sampling is emphasized.

SAMPLING OF FUELS

Coal. Accuracy in the sampling of coal is usually referred to its " ash " content, although moisture is an impurity of equal importance. Strictly speaking, this procedure is not altogether correct since the ash-forming constituents are not uniformly distributed and concordance in ash percentage does not necessarily mean that the coal substance is accurately represented. For this reason some authorities have discussed the accuracy of sampling in terms of calorific value or volatile matter. Since complete accuracy in sampling is not possible and is approached only with considerable trouble, it is apparent that the degree of accuracy necessary will vary with the purpose for which the coal is being handled. It has been considered, for example, that separate samples should agree for export purposes within ± 8 per cent. of the ash content, for industrial purposes within ± 5 per cent. and for power station and experimental purposes ± 3 per cent.

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[1] B.S.I. No. 420, 1931 ; No. 404, 1931 ; 496, 1933 ; 502, 1933.

In dealing with coal the sampler has to contend with widely varying conditions in the size and nature and position of the coal, all of which demand different methods of taking the initial or gross sample. Until recently the only scientific basis for sampling was the experimental work of E. G. Bailey (*J. Ind. Eng. Chem.*, 1909, **1**, 161). This valuable work related, however, more to the reduction of bulk samples than to their obtaining and it was not until 1930 that a scientific theory was advanced to cover the distribution of the small quantities or " increments " of coal which together would give a bulk sample whose ash content would not differ from the true ash content of the consignment by more than a certain amount.

These theoretical questions are fully discussed in papers by Grumell and Dunningham and Grumell and King (*J. Inst. Fuel*, 1933, **6**, 143, and S.T.M. Conf. Zurich, Sep., 1933 ; Eng. Stand. Assoc., 1930, 403). Experience over a number of years had shown these experimenters that each coal had a characteristic variability which could be expressed as the " average error " of ash content of a large number of samples from the true ash content. This average error was found to be the same whether calculated from the increments of one truck, or a number of trucks. Further, the average error was found to increase regularly with increasing ash content for any one coal, though not necessarily for mixed coals.

Each coal has been found to have a characteristic variability which can be expressed as the " average error " of ash content of a large number of samples from the true ash content, and for a given coal the " average error " varies with the ash content approximately as follows :

Average error .	< 1·0	1·0 to 1·5	1·5 to 2·0	2·0 to 2·5
Per cent. ash .	Up to 7	7–10	10–15	Over 15

With mixed coal the " average error " may be as high as 2·5 to 3·0, irrespective of the ash content.

The practical issues are that the total weight of the gross sample taken will :

1. Increase with the ash content of the coal owing to the greater number of increments necessary.

2. Increase with the size of the coal owing to the increase in weight of the increment.

The greatest weight of gross sample is demanded when the coal is large and of high ash content; the smallest by low ash coal of small size.

Full details of the minimum weight of sample for coals of different average ash content and size of coal, as well as detailed instructions for sampling are given in the B.S.I. Specification No. 420, 1931. The following is a summary of the more important points in the procedure.

In taking the increments of coal from a consignment even spacing is the first consideration. When the coal is in motion as in conveyors, or flowing from chutes or hoppers at a uniform rate a time basis is correct; with irregular rates the sampler must assess his increments in terms of tonnage passing the sampling point. The main precaution necessary is to cover with the sampling scoop all parts of the flowing stream since coal tends to segregate into sizes.

Sampling from wagons or heaps is not to be recommended since it is extremely difficult to obtain an average sample. Sometimes it is essential that wagon trains of coal should be sampled; in this case the best procedure is to take the increments from the bottom of holes (1 ft. deep) spaced evenly over the consignments. In doing so it must be borne in mind that the small coal and large coal must be suitably represented in the gross sample since their ash contents may differ widely. In order to do so lumps must sometimes be broken and suitable quantities taken. It is apparent that this method leaves considerable room for error, but it is an interesting fact that an experienced sampler can attain a considerable measure of success when sampling from trucks.

The reduction of the initial or gross sample to one of laboratory size should follow immediately the whole sample is available. Since moisture content is frequently an important factor a coal sample should always be collected by placing the increments in a covered bin so that loss of moisture by either drainage or evaporation is prevented. The bulk sample should be spread on a clean hard floor and mixed, and reduced in weight by crushing, mixing and subdivision. The latter may be done by "coning and quartering" by hand, but preferably with the aid of some mechanical device, such as a "riffle" (see Brit. Stand. Sampling of Coal for Boiler Trials; King and MacDougall, *Fuel*, 1933, **12**, 93). For most of the determinations the air-dried material reduced to pass a 72-mesh British Standard Test sieve is employed.

The underlying principles of sample reduction have been made clear by E. G. Bailey (*loc. cit.*) who first recognized that an important factor was the ratio of the weight of the largest pieces of dirt or shale in the coal to the weight of the sample. This ratio he called the "size : weight percentage," i.e. $100x/w$ where x is the weight of the dirt particle and w the weight of the sample. After exhaustive experiment Bailey drew curves for one coal containing 11·5 per cent. of ash (of which 5·0 was dirt, slate, etc.), connecting the size-weight percentage and the probable and possible errors of ash percentage. In drawing the curves Bailey omitted certain apparently discrepant points and drew what is essentially a curve of mean values. Also, although his papers quote "the size of the largest particle" he actually used the mean of a number of the largest particles.

It must be pointed out that Bailey's findings refer to coal of 11·5 per cent. ash content, i.e. 5 per cent. free ash and 6·5 per cent. inherent ash. It has been accepted that British coals have only about 4 per cent. inherent ash so that a British coal corresponding to Bailey's would contain only 9 per cent. of total ash. Bailey's found errors can therefore be applied directly to British coal of 9 per cent. ash. From this base-line the errors for other coals can be calculated from the finding that the error is proportional to the square root of the free ash content.

It is possible to draft tables connecting weight of sample with each size of coal for a series of S.W.R. or maximum errors. Such tables are of great value in the reduction of samples, but their use is subject to two reservations:

(i) The errors in each stage of reduction may be additive in one direction; reduction in one stage to very small size is therefore a safer method if practicable.

(ii) If the dirt in the sample is hard the largest particles after crushing may be entirely dirt and not coal, so that the mean weight taken for this size in the graph is too small.

Coke. The sampling of coke conforms to the same rules as that of coal. From the point of view of ash content metallurgical coke is less variable than coal since it is normally made from coal crushed to pass a $\frac{1}{8}$-in. screen and well mixed. Gas coke made from larger coal is more similar to coal. Experiment has shown that the moisture content of metallurgical coke is a more variable factor than ash content and the sample necessary for a given accuracy has been deduced from a consideration of the variation of moisture content in the same way as described above for coal. Variation in moisture content increases with the percentage up to 9 and remains constant between 9 and 15. Variation in ash content is less than this except when the moisture content is about 2 per cent. It has been found by experiment that an increment of 2 lb. is satisfactory in sampling coke. The number of increments necessary to give a satisfactory bulk sample varies, therefore, with moisture content. The British Standard Specification (496, 1933) should be consulted for further details. This specification stipulates double samples for cokes other than those containing not more than 10 per cent. below 2 in. and not more than 5 per cent. of moisture or graded coke. The number of 2-lb. increments specified for graded coke so that in 99 cases out of 100 the error in moisture content will not differ from the true value by more than 1 per cent. is :

Moisture per cent.	Number of Increments.
Up to 2	20
2–3	44
3–4	74
4–5	95
5–6	112
6–7	118
7–8	126
8	136

In reducing samples of coke for analysis special precautions must be taken to avoid increase of ash content, owing to the abrasive character of coke.

Oil. The sampling of oils or liquid fuels is not by any means as complicated as in the case of solid fuels, for in general the liquid is of much more uniform composition. Sampling has normally to be carried out either from tanks, barrels, etc., in which the oil is stored or when the oil is in course of transfer from storage to some other position. Nevertheless, certain general principles must be adhered to so that properly representative samples may be obtained, and full directions for sampling of petroleum and petroleum products will be found in the I.P.T. *Standard Methods of Testing* and in A.S.T.M. D.270/33. In the case of oil in flow, arrangements may be made for the collection at intervals of samples which will then be mixed, and an appropriate final sample drawn, or a continuous sample may be taken from the pipe line. In the latter case, in order that it may be average, it is recommended that three tubes, each provided with a stopcock, shall be let into the pipe line, one to the centre, the second to half-way between the centre and the wall of the pipe and the third just through the wall. In this way an average sample of the oil flowing through the pipe is obtained.

Where the material is in vessels which permit of it being thoroughly mixed, this should be done before sampling, but it is obviously impossible with large tanks or receptacles which are practically filled.

From tanks, drums, etc., samples are best obtained by means of a " thief "—usually a metal cylindrical tube of about 1¼ in. diameter with ends tapered off to openings ⅜ in. to ¼ in. in diameter. By plunging this into the oil, allowing it to fill and closing the top opening with the thumb, the sample can be withdrawn.

From tanks an all-levels sample is taken by sinking a weighted bottle in the tank, the bottle being provided with a cork which is *easily removed by means of a line, and raising the bottle to the surface* at such a rate that a fair sample is withdrawn throughout the depth of oil. In the case of deep tanks, drums, etc., samples are drawn at the bottom about the middle and near the top in a similar manner, but the proportion of each quantity taken to make the bulk sample will depend upon the cross-section of the tank. In the case of a vertical cylindrical or a square tank of uniform cross-section, one volume of the upper dip, one of the lower and three of the middle are taken as an average when mixed, whilst from a full horizontal cylindrical tank eight parts of the middle sample are taken to one each of the upper and lower samples.

For the sampling of tar, which is always heterogeneous, special procedure has been developed by the Fuel Research Division. The main stream and the sample stream are arranged to discharge through orifices having the same relation between pressure and rate of discharge whatever the rate. The pressures at the orifices are kept equal and time lag is prevented. If solid matter is likely to cause clogging of the orifices a filter of the " auto-clean " type is used.

For closing receptacles containing oil samples, sound wood corks should be employed, rubber is inadmissible and no sealing by wax or paraffin poured over the corks is permissible.

Certain petroleum samples stored in glass bottles require protection from light.

Gases. The obtaining of a gas sample from a flowing stream of gas of uniform quality or of uniform speed is a relatively simple matter. Special gas-sampling tubes are used which are cylindrical glass vessels drawn out at each end to take glass stopcocks, preferably of the 2-way type. In taking the sample, the tube is filled with a containing liquid and attached to the sampling cock with rubber tubing. If the gas is under pressure it is allowed to blow out of the side tube of the upper stopcock in order to displace air from the connections. Both stopcocks are then opened and the containing fluid allowed to run out of the sampling tube. If the gas is not under pressure, it is necessary to use a suction ball to clear the connection. In some cases where it is inconvenient to use a containing liquid, a suction ball may be attached to the lower stopcock of the sampling tube and the sample drawn through by suction. In this case sufficient time must be allowed to elapse to clear out the air completely.

If the gas stream is not uniform in rate or composition, the gas-sampling tube can be filled by means of a device which lowers the level of the liquid in it at a regulated rate. This may be done by clockwork, the weight of the clock being a levelling tube attached to the lower stopcock, or it may be done by water displacement, the levelling tube being connected to a float in a water tank in which the level of the water is made to rise at a uniform rate (T. Gray, *J.S.C.I.*, 1913, **32**, 1092).

When the main gas stream is being passed through a gas meter, a uniform sample may be collected by gearing a small meter to the drive of the large meter and by-passing through the small meter an aliquot portion of the main stream. In such cases the gas sample is usually measured and is collected in a small gasholder.

The only really satisfactory containing liquid for gas sampling is mercury. Even this is affected by gases which contain hydrogen sulphide. Water and aqueous solutions introduce difficulties, since they dissolve carbon dioxide readily. Saturated solutions of magnesium chloride and 50/50 solutions of glycerine in water have low solubilities for carbon dioxide, and can be used for periods of several hours without causing appreciable errors.

For further information see *Technical Gas Analysis*, by G. Lunge (revised and rewritten by H. R. Ambler), published by Gurney & Jackson, London, 1934.

ANALYSIS OF COAL

For details of the methods of analysis of coal the reader is referred to the British Standard Specifications and to standard text-books such as that of G. W. Himus (*Fuel Testing*, Leonard Hill, Ltd., London).

Formerly, requirements in the way of analysis for fuel use were only the "proximate" analysis, the percentage of sulphur, and calorific value. For special applications, however, the examination of coal embraces also "ultimate" analysis, assay, washability, nature of ash and its fusion temperature, proportion of banded constituents, caking index, softening temperature and certain specialized tests. It would be impossible to describe these fully in this volume, and it has been arranged to take the methods themselves as read and to describe instead certain important facts which are the essential bases of the methods adopted, but which do not appear in the bare details of manipulation.

Coal used for analytical purposes should be ground to pass a 72 B.S. sieve, air-dried and thoroughly mixed. The bottle in which it is stored should be air-tight and quite full. If it is subjected to much handling before analysis the contents should be re-mixed before any portion is withdrawn.

Proximate Analysis. This consists of the determination of moisture, volatile matter, fixed carbon, and ash and sometimes also sulphur content. The moisture figure may sometimes be that of the coal "as sampled" in which case a separate determination must be made on coal which is so treated as not to lose moisture. The proximate and other analyses should always be made on coal which has been air-dried in the laboratory so that its moisture content is in approximate equilibrium with the atmosphere. Changes in moisture content during weighing, etc., are in this case less likely to introduce errors. The precaution is only partial, since atmospheric humidity shows sometimes large changes, and when the analysis is spread over several days the moisture content should be checked more than once per day. The most common method of determination of moisture is that of loss of weight on drying in an oven at 107 ± 2° C. The average oven is badly designed since it contains too large a free space and efficient sweeping out of the moisture-laden atmosphere is difficult. Similarly, when oxidation must be prevented by using an atmosphere of nitrogen, it is practically impossible to achieve this. The only oven which will allow of this method giving the true result is one in which the free space is reduced to a minimum and the coal is heated in a current of nitrogen. Such ovens are only just coming in, and it will not be long before drying in nitrogen will entirely replace drying in air. When coal is heated in air at 107° C. it will first lose moisture and then begin to gain in weight owing to oxidation. Some coals show this phenomenon within the time specified in moisture determinations and therefore the observed loss in weight is less than the true moisture.

The true moisture in coal is obtained by using a nitrogen oven and also when the coal is distilled with toluene in an apparatus similar to that in Figure 71. Both methods in careful hands give results which agree with that obtained by the direct method of weighing the moisture liberated by passing a stream of dry nitrogen over coal heated to 107° C., the moisture being collected in a tared tube containing calcium chloride.

Volatile Matter, Coke, Fixed Carbon. Since the determination of volatile matter in coal is an empirical test it is of the greatest importance that the stipulations of the standard method should be carefully followed. The important factors are rate of heating and temperature used. The coal (1 gm.) is heated to 965° C. ± 15° C. out of contact with air in a crucible of standard size. Formerly platinum crucibles only and gas heating were used, but it has now been found possible to obtain the same results by using silica crucibles in a muffle furnace. The platinum crucible is the ultimate standard, however, and any muffle used must have sufficient reserve of heat so that the introduction of a batch of crucibles does not reduce its temperature so much that it does not recover the full temperature within the coking time. Otherwise, the figure obtained for volatile matter will be low.

Carbonaceous coals and anthracites do not give satisfactory results by the crucible method and should be treated by the method used for coke (see below). Coking in a current of hydrogen by Rose's method will give fairly concordant results.

Some coals tend to decrepitate when heated rapidly and give high results. These must be heated more slowly at first and then at the full temperature. This expedient affects the result to a variable extent, generally in the direction of giving low values.

Before the introduction of the B.S. specifications volatile matter was determined at 925° C. The increase of temperature of 40° C. causes a relatively small increase in the figure obtained; in coal containing 35 per cent. of volatile matter the difference is only about 0·3.

The residue from the determination of volatile matter is referred to as the "crucible" coke or coke button and its appearance gives an indication of the caking power of the coal. In quoting a proximate analysis the analyst should always describe the coke. Unfortunately, the appearance of the coke differs sometimes, depending upon whether a gas-heated platinum crucible or a muffle-heated silica crucible is used: the method of making the coke should therefore be quoted also.

The coke comprises "fixed carbon" and ash, the former being an empirical figure obtained by deducting from the coke percentage obtained in the volatile matter test the ash percentage obtained by the standard method of ash determination.

Alternative methods for the determination of volatile matter are the high-temperatured distillation methods of Bone and Silver and of Lessing. These methods, embodying great control of the rate of heating and the temperature offer some advantages over the crucible method, particularly as regards the definition of the nature of the coke and the correlation of the volatile matter (gas and tar) to carbonization processes. It has been shown that the Lessing method gives figures for volatile matter which are closely related to those of the crucible method. The details of these methods are also given in the British Standard specifications.

Ash. A most important factor in the determination of ash content in coal is that there should be free circulation of air over the coal during its combustion. A second is that initial combustion should be slow in rate since some coals tend to spit or decrepitate. The reason for free circulation of air is to make certain that the inorganic constituents should be fully oxidized. Ash dishes should not be covered during burning off since this increases the amount of sulphur fixed in the ash when the latter contains much calcium oxide.

It is apparent that the ash weighed is less than the original inorganic constituents present in the coal by (i) the CO_2 evolved from carbonates, (ii) the water of hydration of clays, (iii) the change in state from pyrites FeS_2, to iron oxide Fe_2O_3, (iv) the fixation of organic sulphur in the ash as sulphate, and (v) the evolution of chlorine. Some small loss of alkalies may also occur, but not to any large extent if the temperature does not exceed 800° C. Ashes should not contain sulphides if the coal is burned in the proper way with free access of air.

The proportion of inorganic constituents (M) in the coal may be calculated from the ash content by the formula.

$$M = 1{\cdot}09 \text{ ash} + 0{\cdot}5\, S_{\text{pyr.}} + 0{\cdot}9\, CO_2 - 1{\cdot}1\, SO_{3\text{ash}} + SO_{3\text{coal}} + 0{\cdot}5\, Cl.$$

This formula assumes that the water of hydration of clays is 8 per cent., that 3 parts FeS_2 form 2 parts Fe_2O_3 and that half the chlorine is inorganically combined.

A convention such as this is useful in calculations of the true composition of the coal substance, free from inorganic matter, since the inorganic matter may differ from the ash by several per cent. and the use of the ash figure would involve large errors in, say, the true carbon content of "pure" coal.

The composition and fusion temperature of coal ash is of importance when the coal is to be used in a furnace. The methods of analysis are those normally used for silicate rocks and may be found in the paper by King and Crossley (*Fuel Research Tech. Paper* 23, 1928). Fusion temperature was first determined by comparing the behaviour of a cone made of the ash when heated in a furnace alongside Segar cones of known melting-point (Cobb, *J.S.C.I.*, 1904, 11). The more precise method of moulding a small quantity of coal ash into a cone and heating it to the fusion-point under controlled conditions, while recording the temperature, was first examined by Fieldner, Hall, and Feild (U.S. *Bur. Mines Bull.* 129, 1918).

Two temperatures are observed: (i) the initial softening of the test piece and (ii) the final settling of the fused cone to a blob. In the case of ashes which contain iron oxide the nature of the atmosphere over the ash affects the result. An atmosphere which is sufficiently reducing to reduce the iron oxides to the ferrous state gives the lowest fusion temperature obtained. Stronger reduction to free iron gives a higher fusion temperature as does also oxidation to ferric oxide. The atmosphere which gives the minimum fusion temperature varies with the type of ash but may vary between such wide limits as 80 and 20 per cent. of oxidizing gases. Oxidizing gases are oxygen, carbon dioxide and water vapour, while reducing gases are methane, carbon monoxide and hydrogen. A suitable reducing atmosphere can therefore be arranged in several ways; two convenient ways are (1) by introducing cooled flue gas and (2) by burning over the ash hydrogen saturated with water at 80° C., i.e. a 50/50 hydrogen-steam mixture. The difference in temperature of fusion caused by the atmosphere may be very considerable.

In reporting ash-fusion temperatures it is customary to describe the successive stages of deformation of the cone.

A similar method has been developed in this country by Blackie, King and Millott (*Fuel Research Tech. Paper* 23, 1929) which has been shown to give results comparable with those obtained by Fieldner's method. The "cone" used is a 3-sided pyramid about 1 in. high, and with one side vertical, and weighing about 0·7 gm. The temperatures are observed by means of a hot-filament pyrometer, the filament being focused on the tip of the cone. For further details the two papers should be consulted.

Other methods give reliable observations also. The most important is that of Bunte and Baum (*Gas Eng.*, 1932, **49**, 639) in which a graph is drawn of the shrinkage of the test-piece of ash.

Ultimate Analysis. By this is meant the determination of the percentages of the chemical elements which form the coal substance. The methods adopted are therefore very similar to those used in ordinary organic analysis.

The determination of carbon and hydrogen is done on a very small quantity of coal (200 mgm.) and it is therefore necessary to observe certain precautions other than those of the standard method. The chief are that the coal sample should be carefully mixed before taking the quantity for analysis and that a moisture sample should be taken at the same time so that a correct allowance may be made for this in calculating the results. The figures obtained directly for carbon and hydrogen contain the carbon of any carbonates in the coal and the hydrogen of the water of hydration of clays. The true carbon figure is obtained by deduction, but the hydrogen figure is not usually corrected. It is known that some coals contain an appreciable amount of chlorine so that the use of a silver spiral is theoretically necessary. It will usually be found, however, that the lead chromate used to catch sulphur compounds will trap all but negligible amounts of chlorine also.

King and MacDougall (*Fuel*, 1926, **5**, 33) have shown the carbon-hydrogen determinations can be conducted with uniform accuracy if the oxidation zone is maintained at a uniform temperature of 800° C. and a period of about eighty minutes is taken over the combustion of the coal, i.e. two hours for a complete determination.

The amount of nitrogen is determined by variation of the well-known Kjeldahl method for nitrogen in foodstuffs. Potassium sulphate is usually added to raise the temperature of digestion and mercury and/or selenium powder to decrease the time necessary. Crossley (*J.S.C.I.*, 1932, **51**, 237 T.) has obtained satisfactory results using selenium and with digestion times of only one hundred and twenty minutes, eighty of which are after the solution clears.

The amount of sulphur is determined by the Eschka method or by the combustion of the coal in a closed vessel or bomb with oxygen. Both methods are reliable, but certain precautions are necessary in the latter (see King and Crossley, *Fuel*, 1929, **8**, 544). In the Eschka method the flux should not contain more than a trace of sulphur since there is danger that this may not be uniformly distributed.

The sulphur found in this way is the total sulphur and the figure quoted in the ultimate analysis (combustible sulphur) should be less by the amount of sulphur which is fixed as sulphate in the ash. This latter amount is determined directly in ash prepared under the same conditions as those obtaining during the determination of the percentage of ash.

The proportion of oxygen in coal cannot be determined directly by any reliable method and it is customary to obtain this as the difference from 100 per cent. of the sum of the other determined constituents. To do this as accurately as possible it is necessary to calculate, as shown above, the analysis to a mineral matter free basis. This is not always done at present, but should eventually become common practice.

Elements not normally present in appreciable quantity do not appear in the "ultimate" analysis, but their proportion has frequently to be determined. These are chlorine, phosphorus and arsenic. Chlorine is determined by a variation of the Eschka method or by the Carius method for organic substances. Phosphorus is determined in the ash by a modification of the phosphomolybdate method and arsenic by the Gutzeit method.

The results of a coal analysis should always be reported in such a manner as to include both the actual analytical figures and the analysis of the coal as it was used or, failing this, as it was delivered to the laboratory. Calculations to dry coal or to dry ash-free coal should be made only if specially required. The misleading nature of the latter is now recognized. An example of a completely corrected analysis is given below:

	Per cent. as analysed.
Moisture	5·1
Ash	6·2
Carbon	75·4
Hydrogen	5·2
Sulphur (combustible)	1·5
Nitrogen	1·5
Difference	5·1
	100·0
Carbon dioxide	0·3
Sulphur in ash	0·2
Chlorine	0·2
Spyr.	0·6
Sulphate	0·2

	Per cent. as corrected
Moisture	5·1
Inorganic matter [1]	7·1
Carbon [2]	75·3
Hydrogen	5·2
Sulphur (combustible) [3]	1·5
Nitrogen	1·5
Chlorine [4] (organic)	0·1
Oxygen [5]	4·2
	100·0
Total sulphur	1·7
Carbon dioxide	0·3
Total chlorine	0·2

[1] Calculated as shown under ash on page 346.

[2] Total carbon less carbon in carbon dioxide.

[3] Total sulphur less sulphur in ash.

[4] The true correction is as yet uncertain, but there are indications that about half of the chlorine is organically combined.

[5] This is still a difference figure but is more nearly the true oxygen content than the difference figure shown in the "as analysed" column.

In order to make the calculation from ash to inorganic matter it is necessary to determine in the coal the amount of pyrites and sulphate present. The methods adopted are due to Powell and Parr (*Univ. Ill. Bull.* 111, 44, 1919) and are based upon the solubility of sulphates and not pyrites in dilute hydrochloric acid. The sulphate and pyritic sulphur are determined together by digestion of the coal with nitric acid. Organic sulphur is determined by difference.

Special Tests Supplementary to Coal Analysis. Bituminous coals are put to so many diverse uses that their characterization by proximate and ultimate analysis is not always sufficiently accurate. For this reason a number of special tests have been devised for coal to be used for certain purposes. Most of these tests are empirical and depend for their success upon the close application of standardized conditions.

The caking index of a coal may be determined by the Campredon method. The coal is mixed with graded sand (52–72 B.S.I. screens) and carbonized in the same platinum crucible used in the determination of volatile matter. The limiting proportion of sand to coal which gives a coherent coke without forming more than 5 per cent. of dust is the caking index. The sand should have irregular grains and be washed with mineral acid and roasted at 900° C., but even then the test tends to give irregular results. Results are usually quoted over a range such as 15–20, 20–25, in view of this irregularity.

Carbonization assays have been devised to differentiate between coals with special reference to carbonization. In one case, the Gray-King assay (*Fuel Research Tech. Papers* 1, 21 and 24) the method is used in a general sense in coal classification in that it has been adopted by the National Survey of coal seams. One form of the assay has also been adopted for a similar purpose by the U.S. Bureau of Mines. The assay consists in the controlled distillation of 20 gm. of coal as shown in Figure 67. The appearance of the coke gives a valuable indication of caking power. Since the coal treated is a powder, absence of caking power gives a pulverulent coke; medium caking power (about 16 Campredon) gives a " standard " coke about the same volume as the original coal and strong and hard; great caking power is assessed numerically by the proportion of electrode carbon which must be added to give the " standard " coke.

The Gray-King assay has been developed for the assay of gas-making and coking coals ((*Tech. Paper* 24) and is now widely used for this purpose. Other methods of the same type are those of Lessing (*Fuel*, 1923, 2, 152), Fischer (*Gas. Abhandl. z. Kenntniss der Kohle*, 1920, 5, 55), Bauer (Kattwinkel, *Fuel*, 1926, 5, 347), whose method has been elaborated by Muschenborn and Litinsky, and the U.S. Steel Corporation (*Sampling and Analysis of Coal*, p. 76). All of these are,

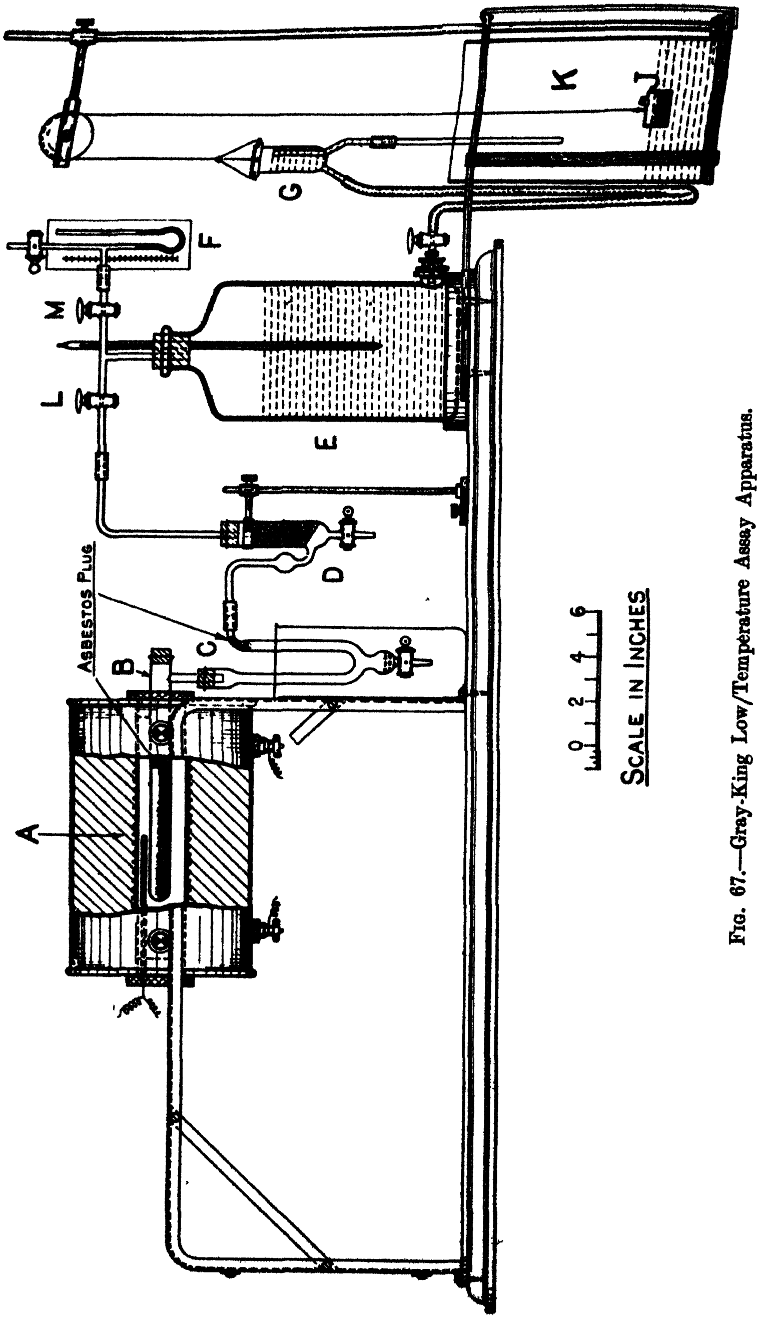

FIG. 67.—Gray-King Low/Temperature Assay Apparatus.

like the well-known one-thousandth ton assay of the gasworks, correlated to plant results.

The behaviour of coal on heating has been the basis of a further group of laboratory methods for the *evaluation of coking coals. These* have measured the melting-point of coal or its softening temperature or swelling power, all of which are significant in coke manufacture. The most important of these are the melting-point method of Audibert (*Fuel*, 1927, **6**, 131), the penetrometer methods of Greger, Dame and Agda and Von Lyncker (*Brenn. Chem.*, 1929, **10**, 86), the degree of swelling method of Mott and Wheeler (*Coke for Blast Furnaces, loc. cit.*) and the swelling pressure method of Jenkner (*Fuel*, 1931, **10**, 232).

The reader is referred to these papers for information as to the details of the methods, and to *Coke for Blast Furnaces*, by Mott and Wheeler (Colliery Guardian Co., London, 1930).

The researches of Wheeler and his co-workers have led to a further method for the analysis of coal which has been called the "rational" analysis (Francis and Wheeler, *J.C.S.*, 1931, 586). In this analysis are determined the proportions of (*a*) free hydrocarbons and resins by extraction with pyridine, (*b*) ulmins by oxidation and extraction with caustic soda, and (*c*) residue. The reactivity of the ulmins is also determined. This method has not yet been widely applied but should become very useful when its findings become more familiar to the technologist.

Accuracy of Coal Analysis. Finally, it is desirable that the reader should have some idea of the accuracy of the results obtained in coal analysis. This subject has been examined by the Fuel Research Division (Survey Paper 29, 1933), who have defined the probable error of the determinations and the amounts by which the means of two determinations may differ from the true result. Certain of their findings are quoted below. The probable error of a determination is a measure of its precision; a given value A has a probable error of "*e*" when it is a 50/50 chance that the true value lies within A + *e* and A − *e*.

	Probable error.	Accuracy of mean of duplicates.	
		Odds 10 : 1	Odds 100 : 1.
Moisture	0·044	± 0·08	± 0·12
Volatile matter	0·072	0·13	0·19
Ash	0·035	0·06	0·10
Carbon	0·138	± 0·25	± 0·37
Hydrogen	0·042	0·08	0·11
Nitrogen	0·020	0·04	0·05
Sulphur	0·014	0·03	0·04
Difference	0·152	0·27	0·42
B.Th.U. per lb.	24·9	44	67

The probable error is, of course, smaller than the possible error which may occur in the usual laboratory practice of meaning two results. The accuracy of such means is assessed in the second column at odds of 10 : 1 and in the third at odds of 100 : 1. These odds are in favour of the true value being within range of mean result ± the amounts shown. The figures are in some cases disappointing, but in others indicate that the standard methods in use are satisfactory. The probable error of calorific value determination is, for example, rather high as stated and should be more nearly 10–15.

ANALYSIS OF COKE

The methods of proximate and ultimate analysis of coal are also those used for coke with the exception of volatile matter. The percentage of volatile matter in coke is so low that it does not prevent oxidation if the crucible method is used and high results are obtained. To obtain more correct figures the coke must be heated in an atmosphere of nitrogen as described by King (*Gas Engineer*, 1930, 47, 517).

Physical tests play an important part in the examination of coke; these are true specific gravity, bulk density, shatter test and abrasion test. The shatter and abrasion tests are used to ascertain the liability of the coke to breakdown on handling.

Details of the methods of analysis of coke can be found in British Standard Specification 496, 1933 with the exception of the abrasion test which is described in *Coke for Blast Furnaces*.

EXAMINATION OF LIQUID FUELS

Standard methods for the examination of petroleum products have been drawn up in this country by the Institution of Petroleum Technologists; in many cases the methods of the American Society for Testing Materials having been adopted. The methods outlined are in accordance with these (I.P.T.) standard methods.

Specific Gravity. This may be taken by any of the usual methods, but with very thick oils is determined best in a 250-c.c. graduated flask, the weight of which and the water content have been ascertained previously.

In many cases, with heavy fuel oils, the weight delivered is computed from the volume, and temperature will be clearly of the greatest importance. It is usual to make a correction of ± 0·0006 to the specific gravity for each degree above or below 15° C. The coefficient of expansion for different petroleum distillates has been given on page 154.

The specific gravity at 15° C. having been ascertained, the weight of the barrel of oil, whether in United States or Imperial gallons, can be calculated.

Flash-Point. This is defined as the lowest temperature at which vapour is given off from the oil in sufficient quantities to be ignited by a flame.

The *Fire Test* or *ignition-point* is defined as that temperature at which sufficient vapour is given off not only to be ignited, but with sufficient rapidity for the oil to continue burning.

This must not be confused with the Spontaneous Ignition Temperature (S.I.T.) which is the temperature at which ignition occurs when an inflammable liquid is allowed to fall in drops into a hot metal crucible.

Clearly the flash-point will be dependent upon, first, the vapour pressure of the oil, which to a minor degree will be dependent on the barometric pressure; secondly, the proportion of oil vapour in air requisite to form an ignitable mixture. This proportion will vary little for the different petroleum distillates, but several factors will determine when the requisite quantity is reached. If the apparatus is open to the air it will be reached only at a higher temperature than in an enclosed apparatus. In the latter the ratio of the air space to the surface of oil exposed will influence the result, so that standard sizes for closed testers must be adhered to rigidly if results are to be comparable. Again, in a closed apparatus, when the test flame is lowered through the testing port, the air and vapour inside are replaced by fresh air drawn down through the other open ports provided, and if testing is performed at regular temperature increments, but at different rates of heating the time given for sufficient vapour to diffuse into the air will vary and hence also the result.

These points are mentioned in order to emphasize the necessity for adopting standardized apparatus and procedure, if discrepancies are to be avoided.

The *open flash test* is clearly liable to considerable variation and is only an approximate test, though often of value for lubricating oils some crude oils and residues. The I.P.T. standard method is to use the cup of the Pensky-Marten tester, the cover being replaced by a clip around the rim arranged to carry the thermometer and test flame. The thermometer is fixed at the centre of the cup, and the centre of the bulb must be ½ in. below the filling line. The apparatus must be carefully screened from draughts, the oil must not be stirred, and the rate of heating must be approximately 10° F. (± 1°) per minute.

The United States (A.S.T.M.) open test is carried out in a special shallow brass cup—Cleveland open cup, 2½ in. internal diameter and $1\frac{5}{16}$ in. internal depth, the filling mark being ⅜ in. below the rim.

Closed Tests. The *Abel apparatus* has become a legally standardized tester in this country and the Colonies, and is employed for ordinary burning oils. The apparatus, together with dimensions for the principal parts is shown in diagrammatic section in Figure 68. The cup A is insulated from direct contact with the heating vessel B by a vulcanite ring *v*, on which the flange rests. There is an air space C ½ in. across between the sides and bottom of the cup and the wall of the heater, so that with water always at one temperature in the latter when commencing, the rise of temperature of the oil is always regular, though not uniform for equal increments of time.

The procedure for legal testing is laid down strictly, but need not be detailed here. For ordinary purposes the following directions will suffice:

The heater is filled with water at a temperature of 130° F. The oil cup is placed on a level surface and filled to the proper level, care being taken that none is splashed on the sides.

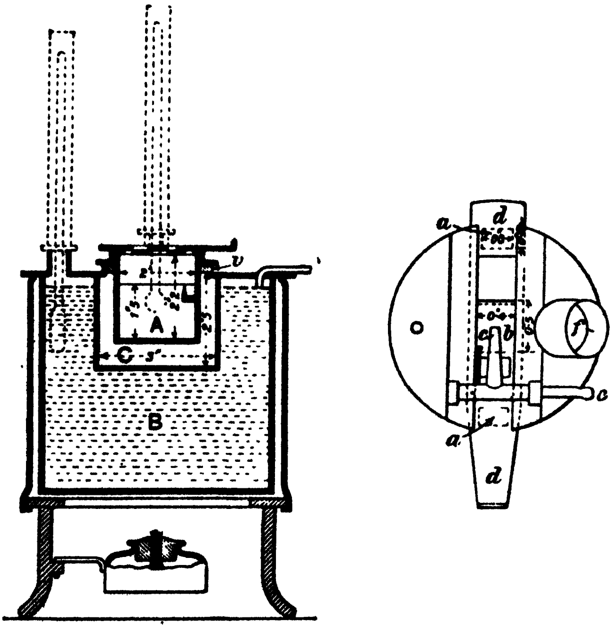

FIG. 68.—Abel Flash-point Apparatus.

The cover is placed on the oil cup, the thermometer inserted, and the test flame adjusted to the size of the bead provided and mounted on the cup.

The cup is placed carefully into position in the heater, the whole apparatus being in a situation free from draughts. Testing is commenced at 66° F., the slide being drawn open *slowly* and closed *quickly*. This is repeated at every degree rise of temperature until a flash is obtained.

If a flash occurs between 66 and 73° F. (the lower legal limit) a fresh portion of the oil is cooled to 55° F. before putting in the cup, and testing is commenced at 60° F.

If no flash is given before 90° F. the bath is emptied and refilled with water at 90° F., also the air space to a depth of 1½ in.; fresh oil is taken, and the whole warmed up by the burner, testing being carried out at degree intervals.

With very low flashing oils the sample may be cooled to 32° F. in melting ice, also the oil cup itself, before filling. The cup may be mounted conveniently through a sheet of asbestos card, so that it extends into a beaker containing water (with ice) at 32° F. If there is no flash under these conditions the temperature is raised slowly until the proper flash-point is reached. A special thermometer will require to be fitted by means of a cork, as the one supplied with the apparatus does not record these low temperatures.

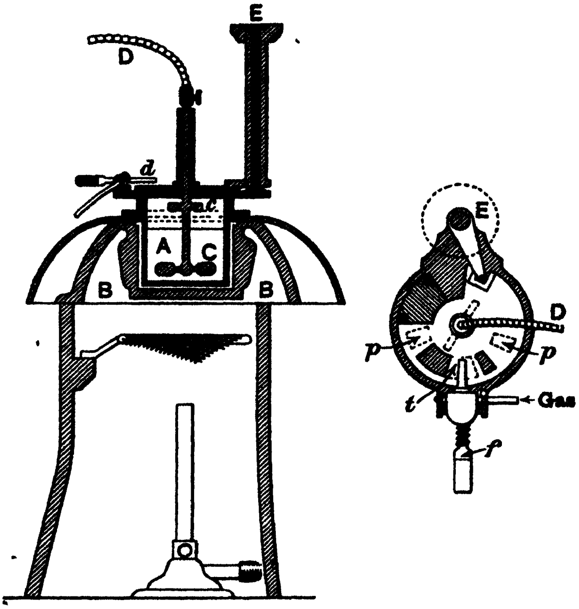

Fig. 69.—Pensky-Marten Flash-Point Apparatus.

A, Oil cup ; B, Cast-iron heater ; C, Oil stirrer ; *c*, Vapour stirrer ; D, Flexible wire to operate stirrer ; E, Milled head for operating cap ; *d*, Test jet ; *f*, Flame regulator ; *t*, Test flame port ; *pp*, Air ports.

Where special accuracy is demanded, the flash-point is corrected for barometric pressure, 1·6° F. being added or subtracted for each inch above or below 30 in.

The *Pensky-Marten tester* is the most suitable for all oils flashing above 120° F. The construction, dimensions and method of use of these instruments have been agreed between the I.P.T. and the A.S.T.M. With these oils it is necessary to provide a stirrer in the oil, and also one to mix the heavy vapours with the air. A mass of iron is employed instead of water for the heaters. The apparatus is illustrated in Figure 69. The stirrer is operated by means of a flexible wire, and *the cup ports opened, the test flame inserted and the ports closed by turning the milled head on the upright pillar.*

The rate of heating should not be less than 9° F., or more than 11° F. per minute, and the stirrer should be turned approximately one revolution per second. The test flame should be applied at every 2° F. for oils with a flash-point below 220° F. and above this temperature at every 5°. Suitable "low" and "high" reading thermometers are specified. In applying the flame, one half-second is allowed for opening the port, the flame must remain in the testing position for one second, then the port is quickly closed. Stirring must be discontinued during the application of the test flame (I.P.T. standard method).

It is most important with all these testers to see that oil does not remain between the sliding and fixed plates forming the cover. These should be separated and thoroughly cleaned if necessary.

Viscosity.[1] The viscosity of an oil hitherto has been of most importance from the point of view of lubrication. With the extending use of oils for internal combustion engines the viscosity, or mobility, at different temperatures is of increased importance from this wider outlook. For ordinary fuel oils for burning, laboratory instruments are not generally suitable; the orifice or diameter of the tube employed is too small and the head of pressure too low. A practical test through a pipe under a given head of pressure is preferable. The American Navy Board takes a pipe 4 in. diameter and 10 ft. long, and the oil under a head of 1 ft.

The *Redwood viscometer* has been adopted generally in this country for laboratory determinations of viscosity and has been carefully standardized by the I.P.T. It is illustrated in Figure 70. The oil is contained in a central cup, having an orifice at the bottom drilled through a piece of agate. This is kept closed by a simple ball valve until the experimental conditions are realized. The water in the jacket is brought to any desired temperature by a burner placed under the extension limb, and paddles for stirring the water are provided, these centring round the oil cup.

Owing to the bad heat conduction and sluggish convection currents in most oils, it is always advisable to bring the oil to within a degree or so of the required temperature before filling the oil cup. This is done best by using a flask of about twice the volume of oil required for the test, a little more than half-filling with the sample, and immersing in a large beaker of water at the proper temperature. The oil then can be shaken about and brought quickly to the bath temperature.

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[1] In the commercial sense the viscosity of an oil is the time of flow through a given orifice in a specified apparatus at a given temperature. Hence it is a function of the apparatus, whilst the true viscosity is independent of the form of apparatus.

Having filled the cup to the top of the gauge point and obtained the correct temperature, the ball valve is opened, and 50 ml. of oil run into a graduated flask placed below, the time being taken by a stop-watch. The flask should not be insulated in any way. Viscosity determinations are usually made at one or more of the following temperatures: 70°, 100°, 140°, 200°, 250° F. In the latter case oil is used in the heating bath.

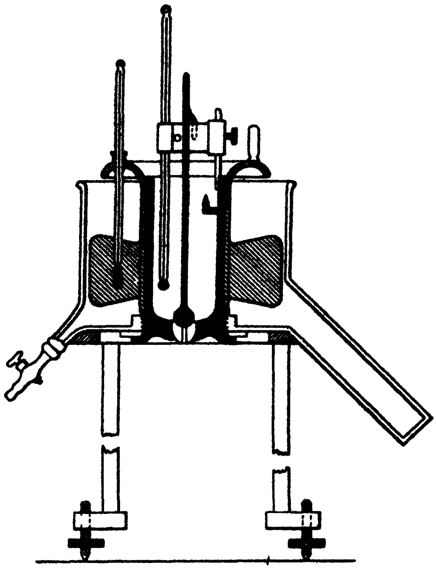

FIG. 70.—Redwood Viscometer.

The above instrument is known as *Redwood No. I*, and is employed for all oils with an efflux time of less than 2000 seconds at the temperature of test.

For oils of greater viscosity the *Redwood No. II* (or Admiralty pattern) is employed. This instrument is designed to give ten times the rate of flow of the Redwood I, and is therefore only suitable for oils of high viscosity.

It is similar in design to the above, but the oil flows through an agate tube 5 cm. long and about 3·5 mm. diameter. The oil cylinder is raised on legs so that it and the full length of the agate tube are surrounded by the heating medium contained in the outer vessel. Each instrument has to be standardized by experiment.

In technical work the viscosity is usually expressed as the number of seconds for 50 ml. of oil to flow through the instrument at the stated temperature (F.°). It should also be stated whether in Redwood No. I or Redwood No. II.

A method for determining the viscosity of oils in absolute units will be found in B.S.I. Specification No. 188, 1929.

Water in Oils. Distillate fuel oils should be free from water and solid suspended matter, but residue fuel oils often contain these impurities, and their estimation is of importance. Water and sediment may be estimated together by dilution of the oil with an equal volume of 90 per cent. benzole and allowing the mixture to stand several hours in a suitably graduated measure, or by centrifuging the mixture. Special measures with a narrow graduated lower portion are made for this test.

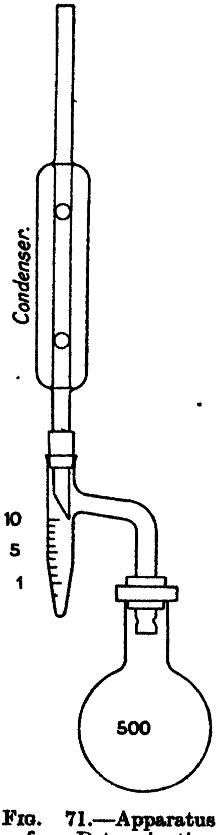

Fig. 71.—Apparatus for Determination of Water in Oils.

Water is most accurately determined by distillation after 100 c.c. of the oil has been diluted with 100 ml. of a high-boiling petrol (5 per cent. distilling below 100° C. and 90 per cent. below 205° C.). The distillation may be carried out in an ordinary 500 ml. distillation flask and the distillate received in a graduated receiver. The distillation is continued until a thermometer in the vapour indicates 400° F. and all condensed water has passed into the graduated receiver. A more convenient apparatus is that of Dean and Stark (Fig. 71), in which the reflux condenser passes all the water into the special graduated receiver and the condensed petrol overflows back into the round distillation flask.

Distillation Tests. With the exception of fuels of high vapour tension (petrol, benzole, etc.) distillation tests are not required. For petrol the standard method of the I.P.T. and A.S.T.M. is adopted.

An Engler flask is used, the side lead being connected to a brass seamless condenser tube, 22 in. long, $\frac{9}{16}$in. outside diameter. This is cooled in an ice/water mixture contained in a rectangular bath, 15 in. long. The lower 3 in. of the tube is curved downwards, the end being cut off at an angle. The flask is mounted vertically on a sheet of asbestos, and rests in a hole 1¼ in. diameter. The flask, support, and source of heat must be effectively screened from draughts.

One hundred ml. of the sample are measured into the flask, and the same measuring cylinder is used to collect the distillate. The bulb of the thermometer is adjusted so that the bottom of the capillary is level with the side tube. The flame is adjusted to give a rate of distillation of 4–5 ml. per minute, being suitably increased as distillation proceeds. The initial boiling-point (I.B.P.) is the temperature when the first drop falls from the end of the condenser, and the final boiling-point (F.B.P.) is the maximum temperature the thermometer reaches which is usually when the bottom of the flask is just dry. Distillation tests should record the I.B.P., the volume of distillate collected at 50°, 75°, 100°, 125°, 150°, 175°, 200°, 225° C., and the F.B.P., also the total volume of distillate, the volume of residue in the flask, the loss, and the barometric pressure.

The Standard Method for Testing Tar Products (lower-boiling fractions) is very similar, except that a glass condenser tube 60 cm. long and 1·5 cm. bore is employed, with a water jacket 45 cm. in length. Cooling in this case does not require to be below water-supply temperatures. With petrols, however, especially when casing-head spirit is a component, these temperatures would not ensure efficient condensation.

Sulphur. The estimation may be required in any of the liquid fuels, ranging from petrols to the heavy fuel oils.

For petrols and kerosines the I.P.T. lamp method is employed and this consists in burning 5 ml. in a special small glass lamp of about 25 ml. capacity.

The products of combustion are gently aspirated through a double-bulb U-tube containing 10 ml. of a standard solution of sodium carbonate, diluted with an equal volume of water. This absorbs the oxides of sulphur resulting from the combustion. The sodium carbonate solution contains 3·306 grams per litre. A corresponding strength, hydrochloric acid solution contains 2·275 grams per litre.

After some 4–5 grams of the sample have been burnt, the apparatus is washed out thoroughly, and the sodium carbonate solution titrated with HCl (using methyl orange as indicator). Each ml. of acid used corresponds with 1 mgm. of sulphur.

The Tar Products method differs in many respects—the form of apparatus, the absorbent, which is neutralized hydrogen peroxide, and the estimation of the sulphur, which in volumetric, N/10 sodium carbonate being used. The fuel is mixed with five times its volume of rectified spirit of wine before introduction into the lamp.

For heavy oils the bomb method (see Calorimetry, p. 369) is the standard method. The determination of sulphur is necessary in all cases where the correction of the calorific value for the formation of sulphuric acid during the combustion has to be made.

Alternative methods, however, require mention. Hodgson regards the Carius method, commonly employed in organic analysis, as suitable for accurate results. Goetzl (*J.S.C.I.*, 1905, 1086) places 2–3 grams of the oil in a large platinum crucible, 4 c.c. of fuming nitric acid are *floated on top, the cover put on, and the liquids allowed to mix gradually and then stand over-night. The mixture is heated on the water-bath, and, when action ceases, evaporated to dryness. The dry residue is mixed with 5 grams of dry sodium carbonate and 1 gram of* potassium nitrate, a layer of the same mixture being placed on the top, and the whole heated until white. The residue is dissolved in water, and the sulphur determined.

Garrett and Lomax (*J.S.C.I.*, 1905, 1212) employ a modification of the Eschka method. 0·7 to 1·5 grams of the sample are mixed intimately with 3–4 grams of a mixture consisting of 4 parts of pure lime and 1 part of dry sodium carbonate. The crucible is then filled up with this mixture. A larger platinum crucible is then placed over the smaller one, the two inverted, and the space between the two filled with the mixture.

The mouth of the crucible is covered with a thick pad of asbestos board, and the two crucibles placed in a muffle already heated. The asbestos prevents radiation from the top of the muffle heating the substance until the soda-lime packing is hot. In two minutes distillation commences, the asbestos may then be removed, and heating continued for two hours. The process is completed as in Eschka's method. Results are said to be good when compared with those by the Carius method.

Paraffins and Naphthenes in Benzole Mixtures. A method which is used in the National Benzole Company's laboratories, and which is said to yield reasonably accurate results, depends upon the solution of the aromatic hydrocarbons in 98 per cent. sulphuric acid. The method has the merit of simplicity, compared with the many other methods which have been proposed.

A special mixing and measuring tube is employed, having a cylindrical portion of such diameter and length that it will hold rather more than 20 ml., for which volume the tube is graduated. At either end there is a bulb, the lower one provided with a stopcock, the upper with a stopper.

Eighty ml. of 98 per cent. sulphuric acid are poured into the tube, up to the lower mark on the graduated scale, and 20 ml. of the sample added. The tube is stoppered, inverted and gently shaken, the pressure being released by opening the tap cautiously. Cooling is necessary if the action is too violent. After eight minutes' good agitation the mixture is allowed to stand and the volume of residual spirit read. Shaking is repeated until no further diminution of the volume is noted. After cooling, the volume of "paraffins and naphthenes" is then read.

With mixtures containing unsaturated hydrocarbons, for example, with mixtures containing cracked spirit, treatment with 80 per cent.

sulphuric acid, followed by distillation *to separate high-boiling polymers*, must precede the estimation of paraffins and naphthenes.

Carbon Residue. For fuel oils for internal combustion engines, and also for lubricating oils for similar engines, the amount of carbon (coke) left by heating the oil to a high temperature in the absence of air is important. Results are liable to great variation unless special attention is given to procedure and a standard apparatus is used. For the standard method (Conradson Coking Test) a silica or porcelain crucible, 30 ml. capacity, is placed in an iron crucible 65–82 ml. capacity. This is provided with an iron cover having an opening 5–6 mm. diam. This again is placed inside a large iron crucible (with a lid) 200 ml. capacity. Enough sand is placed in this outer crucible to bring the cover of the inner iron crucible nearly to the top of the outer one. The three crucibles are carried on a triangle and surrounded by a hollow heating block with a short chimney.

Two glass beads about 0·1 mm. diam. are placed in the porcelain crucible and included in its first weight and such a quantity of oil is taken that the coke residue does not exceed 0·4 gram. The apparatus is set up, and heated till vapours ignite, then the heating is moderated to give a flame less than 2 in. high from the top of the short chimney. When vapour ceases to come off, the heat is increased and the lower part of the large crucible is kept red-hot for five minutes. The apparatus is allowed to cool and the porcelain crucible removed, placed in a desiccator and weighed.

An alternative method is that of Ramsbottom, which is included in the Royal Air Force specifications for lubricating oils. It is applicable to distillate fuel oils but is not suitable for asphaltic fuel oils, owing chiefly to excessive frothing. Moreover, results by this method are not strictly comparable with those by the Conradson method.

Approximately 4 grams of the sample are introduced into a glass bulb, which is approximately 38 mm. from the base to the shoulder, where it is terminated in a capillary 9·5 mm. long and 1·5 mm. diam. This bulb fits closely into an iron tube 3 in. long and 1 in. diam., and when the charged bulb is inserted, the iron sheath is lowered into a bath of molten lead, so that not more than ¼ in. is above the surface of the lead. The lead bath is maintained at 550° C., and the bulb is allowed to remain at this temperature for ten minutes after fuming has ceased. It is then cooled, cleaned outside if necessary and weighed.

Hard Asphalt. Asphaltic bodies, such as occur in petroleum, are bodies of a very indeterminate character. Broadly two main classes are recognized—hard asphalt, which is insoluble in light petrols (petroleum spirit), and soft asphalt, soluble in petroleum spirit, but precipitated from an ether solution of the oil by the addition of alcohol. Hard asphalt is regarded as an undesirable constituent of fuel oils for *use in internal combustion engines, and its estimation is required in most specifications.*

The petroleum spirit must be free from benzene and other aromatic hydrocarbons. The I.P.T. specification requires not more than 0·5 per cent of aromatic hydrocarbons and that at least 90 per cent. distils between 60° and 80° C. It should have a specific gravity not above 0·690 (60° F.). To prepare it the spirit having a boiling range of 60–80° C. (by the standard method, p. 358) must be thoroughly shaken with three volumes of strong sulphuric acid (98–100 per cent. H_2SO_4).

Such a weight of oil is taken (not, however, over 10 grams) that the precipitated asphalt does not exceed 0·25 gram, and dissolved in warm petroleum spirit, the quantity used (in ml.) being ten times the weight of oil (in grams) taken. The mixture is allowed to stand twenty-four hours. The solution is filtered through an 11-cm. folded filter and the filter and material washed with the spirit until the washings are colourless. The asphaltic material is then dissolved in benzene, the solution being collected in a weighed conical flask. The benzene is distilled off and the asphalt dried in a steam oven for one hour.

In cases where the asphalt content is high a smaller amount of the sample must be used, for it is undesirable to have more than 0·25 gram of the insoluble asphalt to filter, wash, etc.

Ash. This estimation is important for fuel oils for internal combustion engines. Even more important perhaps than the actual quantity is the character of the ash, a harsh gritty ash being very abrasive in the cylinder.

The usual method of determination in distillate oils involves evaporating down some considerable quantity (250 grams or over), transferring to a platinum dish and continuing the evaporation, and finally igniting until all carbon has been burnt.

Heavy residue oils can generally be evaporated directly in the platinum dish, and this is necessary if they contain much asphalt. In such cases 30–50 grams is usually sufficient for the estimation.

CHAPTER XVIII

DETERMINATIÓN OF CALORIFIC VALUE

Definitions of the units employed and a discussion on gross and net calorific values have been given in Chapter I. Here it remains only to consider methods by which the calorific value may be arrived at. These methods may be divided into those based upon calculations from the heating values of the constituents, or obtained by direct determination in some suitable calorimeter.

Calculated Calorific Values. For coals the calorific value may be calculated on a basis of the elementary constituents, or on the proximate constituents. For oils, on the elementary constituents; for gases, from the values for the individual combustible gaseous constituents.

In calculating on the ultimate composition of the coal it is assumed that the elements have the same heating value as they have in the free uncombined state, and that oxygen is present in combination with its equivalent of hydrogen in the form of water, assumptions which are inherent to the method but certainly not justifiable. It involves likewise the assumption that heat is neither expended nor evolved in rendering the atoms of the constituent elements free to enter into fresh combinations with oxygen on combustion. Since coals low in oxygen have been shown to be only slightly endothermic in formation, it so happens that no heat is demanded for this, which explains the otherwise anomalous fact that calculated results in the majority of cases do agree fairly well with the determined values.

The best-known formula is that of Dulong, of which numerous modifications have been proposed. Its original form was:

$$\frac{8080\,\mathrm{C} \times \left(\mathrm{H} - \frac{\mathrm{O}}{8}\right)34{,}400}{100}$$

where C, H and O are the percentages by weight of these elements.

In its most complete form, with values for carbon and hydrogen due to Berthelot, it becomes:

$$\frac{8137\,\mathrm{C} + 34{,}500\left(\mathrm{H} - \frac{(\mathrm{O} + \mathrm{N}) - 1}{8}\right) + 2220\,\mathrm{S}}{100} = \text{gross calories.}$$

It being assumed that the oxygen is wholly in combination with hydrogen, the available surplus of hydrogen for combustion is equal to $\left(\text{Total Hydrogen} - \frac{\text{Oxygen}}{8}\right)$. In ordinary analyses oxygen and nitrogen are found usually by difference, and since the average nitrogen content is about 1 per cent., this deduction is made from the "difference," and the remainder $(O + N) - 1$, represents the oxygen.

Net calorific value is not now used in this country but is still in common practice on the Continent. It is found by taking the net calorific value of hydrogen and introducing a correction for heat expended in evaporating any moisture (the round number 600, as approximately representing the latent and sensible heat in the steam at 100° C.), the formula becomes modified further to:

$$\frac{8137\,C + 28{,}780\left(H - \frac{(O + N - 1)}{8}\right) + 2220\,S - (H_2O \times 600)}{100} = \text{net value.}$$

The modification of the Dulong formula adopted in Germany is:

$$81\,C + 290\left(H - \frac{O + N}{8}\right) + 25\,S - 6\,H_2O = \text{net value.}$$

A simplified formula for the evaporative value from and at 212° F. formerly used in this country is:

$$E = 0{\cdot}15\left\{C + 4{\cdot}28\left(H - \frac{O}{8}\right)\right\}$$

It is derived thus: calorific value of hydrogen is to calorific value of carbon as 34,400 is to 8080 = 4·28; the evaporative value of carbon is $\frac{8080}{100 \times 536{\cdot}5} = 0{\cdot}15$ lb. from and at 212° F.

Whilst with coals of low oxygen content results are generally in good agreement with those determined in a bomb calorimeter, they are often wide of the truth when the oxygen content is high. Brame and Cowan (*J.S.C.I.*, 1903, 1230), found the calculated values were from 0·7 per cent., in the case of an anthracite, to 4·8 per cent. *below* the determined value, in the case of a bituminous coal containing 10·57 per cent. of oxygen. Gray and Robertson (*J.S.C.I.*, 1904, 704) found differences ranging from + 0·9 to − 2 per cent. with a series of 12 coals. Bunte found differences ranging from − 3·7 to + 2·0 per cent., and other results might be quoted.

W. Inchley (*The Eng.*, 1911, **111**, 155) reviews the question of calculated values, and puts forward the following modifications of the Dulong formula as giving more correct results:

$$\text{For solid fuels}\begin{cases} 8000\,C + 33{,}830\,H = \text{gross calories per gram.} \\ 14{,}000\,C + 60{,}890\,H = \text{gross B.Th.U. per lb.} \\ 14{,}000\,C + 52{,}196\,H = \text{net B.Th.U. per lb.} \end{cases}$$

$$\text{For liquid fuels}\begin{cases} 7500\,C + 33{,}830\,H = \text{gross calories per gram.} \\ 13{,}500\,C + 60{,}890\,H = \text{gross B.Th.U. per lb.} \end{cases}$$

Brame has applied the formula for solid fuels to all the coals analysed by Cowan and Brame and by Gray and Robertson in their comparisons of different calorimeters. Results, in percentage difference from the bomb, range from − 2·42 to + 3·8. The formula for liquid fuels gives results in general within 1 per cent. of the determined value. From calculations on the German Dulong formula applied to a series of petroleum oils, W. H. Patterson (*J.S.C.I.*, 1913, 218) found the *net* calorific value from 1·25–4·2 per cent. *too high.* With two tar oils, containing respectively 5·98 and 7·29 hydrogen, the results were 3·85 and 2·97 per cent. *too low.*

The discrepancy between calculated and determined results, which is more apparent when the oxygen content is high, has been recognized by Mahler, who proposed the following formula:

$$\frac{8140\,C + 34{,}500\,H - 3000\,(O + N)}{100} = \text{gross calories}$$

Other formulæ are constantly being suggested. Grumell and Davis (*Fuel*, 1933, **12**, 199) give the following:

$$C = (3{\cdot}635\,H + 235{\cdot}9)\left(\frac{C}{3} + H - \frac{O - S}{8}\right)$$

Calculated values are always open to objection. In the first place, small analytical errors are multiplied largely; secondly, the calorific value for the same element varies somewhat as determined by different observers; thirdly, in the case of carbon, different varieties from different sources exhibit considerable variation in calorific value, depending largely on their density. In addition the state of combination of the sulphur is not constant and thermal changes are introduced by changes in the constitution of the mineral matter. Uncertainty must always exist therefore as to which value should be chosen.

Summarized, the conclusions as to calculated values on ultimate analysis are that although good agreement (say, within 1 per cent.) is found with most coals and liquid fuels, there is always the liability of a far greater error occurring. In view of the much greater labour of conducting the ultimate analysis, which is required so seldom for technical work, and the simplicity of obtaining correct values in a good calorimeter, little can be said in favour of calculated values for solid and liquid fuels. Calculated values can be justified only when facilities do not exist for making an accurate practical determination of the heating value, and when calculated this should be clearly stated.

Calculation from Proximate Analysis. Goutal claims that a relationship between the amount of fixed carbon and volatile matter and the calorific value may be traced in coals. This he deduced for a large number of French coals by comparison with the calorific value determined in a bomb calorimeter, constants for varying amounts of volatile matter being determined. These constants must necessarily be calculated on the dry and ash-free coal, i.e. on the pure combustible. *Goutal's formula is* $82C + aV$, *where* C *represents the fixed carbon,* a *the constant, and* V *the volatile matter found on the whole coal.*

The values for the constant a, *for different values of* V^1 *(the volatile matter in the pure coal substance, which equals* $\left(\frac{V \times 100}{C + V}\right)$ are:

V^1	5	10	15	20	25	30	35	38	40
a	145	130	117	109	103	98	94	85	80

Applied to Brame and Cowan's coals (*loc. cit.*), the errors amount to $-2{\cdot}15$ to $+1{\cdot}88$ per cent.

Taylor and Patterson (*J.S.C.I.*, 1929, **48**, 1051) report values varying from $-15{\cdot}3$ to $+5{\cdot}4$ for a variety of coals, divergence which almost rules the formula out of court.

Constam and Kolbe have shown that with English coals there is often a very wide difference between the heating value for coals containing the same amount of volatile matter, and whilst the heating value of the coke is practically always the same, there must be a big variation in the heating value of the volatile matter, due to difference of composition. Goutal's formula can apply only when there is a definite relation between the heat of combustion of the volatile constituents and their amount. This is frequently the case but by no means invariably, so this method of calculation is unreliable.

Calculation for Gaseous Fuels. In the case of gaseous fuels, in such mechanical mixtures the constituent gases preserve their heating value, and the calculated results are accurate. Where the gaseous mixtures contain hydrocarbons more elaborate calculations are necessary. In the cases of the saturated hydrocarbons C_nH_{2n+2} the value of "n" is usually determinable in accurate gas analyses and represents the mean molecular weight of the hydrocarbons present. The calorific value of the mixed hydrocarbons is then usually determined by B.Th.U. per cu. ft. $= 995 + (0{\cdot}ab \times 735)$ where $0{\cdot}ab$ is the decimal part of the "n" value and 995 is the calorific value of methane saturated at 60° F. and 30 in. The value for ethane is $995 + 735$, i.e. 1730 B.Th.U. This assumes that the gases are methane and ethane only and is satisfactory for gases in which the "n" value is less than 1·20. In other cases the formula should be C.V. $= \frac{1000(8n + 1)}{4}$ B.Th.U. per cu. ft. saturated at 60° F. and 30 in. In this formula all members of the saturated hydrocarbon series may be present; the calculation involving the fact that the calorific value of oxygen burning in a saturated hydrocarbon gas is constant at 500 B.Th.U. per cu. ft.

Unsaturated hydrocarbons present greater difficulty since their composition is difficult to measure by ordinary gas analysis and a mean value must be assumed for each type of gas. Manning, King and Sinnatt (*Fuel Research Tech. Paper* 19, 1928) *suggest mean values* of (1) high-temperature coal gas and (2) for low-temperature gas as follows:

$$\left.\begin{array}{lll} (1)\ C_2H_4 & \text{two-thirds} & \text{of } 1560 \\ \quad\ C_6H_6 & \text{one-sixth} & \text{of } 3740 \\ \quad\ C_3H_5 & \text{one-sixth} & \text{of } 2300 \end{array}\right\} \begin{array}{l}\text{2050 B.Th.U. per cu. ft. satd. at 60° F.} \\ \quad \text{and 30 in.}\end{array}$$

$$\left.\begin{array}{lll} (2)\ C_6H_6 & \text{one-quarter} & \text{of } 3740 \\ \quad\ C_2H_4 & \text{three-eighths} & \text{of } 1560 \\ \quad\ C_3H_6 & \text{three-sixteenths} & \text{of } 2300 \\ \quad\ C_4H_8 & \text{three-sixteenths} & \text{of } 3040 \end{array}\right\} \text{2520} \quad ,, \quad ,, \quad ,,$$

In other types of gas the proportions would certainly differ and, as the calorific values of these gases are high, lack of knowledge may introduce a large error into calculated calorific values.

Where *accurate* gas analyses are not available direct determination is necessary; in any case it should always be adopted where possible as the direct method. When the gas sample is available only in small amount and a flow calorimeter cannot be used an explosion calorimeter of the Union type is recommended by Blackie (p. 383).

CALORIMETRY OF SOLID FUELS

The general principle of all calorimeters is the transference of the total heat of the combustion of a known weight of the fuel to a known weight of water; from the rise of temperature of the latter the calorific value is deduced. Not only is the water raised in temperature, but the whole of the instrument in contact with it, and it is necessary to know the heat utilized in doing this, measured in terms of water. This is known as the *water equivalent* of the instrument, and must be determined accurately once for all.

For the direct determination of the heating value of fuel certain essential conditions must be fulfilled for accurate results. Combustion must be complete; hence there must be no smoke, no carbon monoxide formed, and no invisible unburnt hydrocarbon gases escaping. The heat must be transferred completely to the water, losses by cooling from the calorimeter must be corrected for, and finally the rise of the temperature of the water must be determined with great accuracy, since the mass of fuel used is very small as compared with the mass of water heated.

Calorimeters may be classified as follows:

1. Where combustion is achieved by admixture of the fuel with a solid oxidizing agent.
   - (*a*) A mixture of nitrate and chlorate of potassium (Lewis Thompson).
   - (*b*) With sodium peroxide (Na_2O_2) (Parr and Wild).

2. By combustion with oxygen at ordinary pressures.
   (*a*) Where the temperature of the escaping products can be ascertained (Favre and Silbermann, Fischer, etc.).
   (*b*) Where the products escape through water, and are assumed to be cooled to its temperature (William Thomson and innumerable modifications).
3. By combustion with oxygen at high pressures (Berthelot-Mahler bomb calorimeter and all modifications).

Comparison of the results obtained with solid fuels in different types of calorimeters against those given in the Berthelot bomb type have shown liability to such errors that in British, German and American Standard Specifications and Methods the bomb type is alone recognized for solid and liquid fuels (B.S.S. 420, 1931; 496, 1933).

Papers dealing with the comparative results with different calorimeters include the Lewis Thompson by Brame and Cowan (*The Engineer*, May, 1905); Lewis Thompson, Wm. Thomson and Fischer by Brame and Cowan (*J.S.C.I.*. 1903, 1230); Lewis Thompson and Wm. Thomson by Gray and Robertson (*loc. cit.*, 1904, 704); the Parr by Constam and Rougeot (*Abs. loc. cit.*, 1906, 108), and the modified Parr, the Roland Wild instrument, by Lloyd and Parr (*loc. cit.*, 1910, 740).

The paper by G. N. Huntley (*J.S.C.I.*, 1910, 917) on the Accuracy obtainable in Fuel Calorimetry should be studied carefully.

With calorimeters using oxygen at, or about, atmospheric pressure combustion is rarely complete, seldom is some smoke absent in the case of coals and heavy fuel oils are even worse. In some of the earliest determinations this was observed and Favre and Silbermann in their classical experiments always passed the products of combustion through a heated copper oxide tube and made corrections for the partially burned products.

One very obvious point, to which it is only necessary to draw attention because it is overlooked so frequently, is the absurdity of returning calorific values to the first and even second decimal place. It is clear that the last significant figure has no real value, even in the most accurately conducted tests.

Probable variation in the sample examined from the bulk of the coal from which it is drawn is of much greater order than the errors in calorimetry with the bomb apparatus. It is clearly very essential to take every step possible to reduce the sampling variation to a minimum.

For a proper estimate of the value attaching to calorimetric values it is essential to know the method by which the result has been arrived at, and this should be stated in every case. In the literature on fuels this has been exceptional.

BOMB CALORIMETERS

These are all developments and modifications of the original "bomb" pressure calorimeter, which Berthelot employed first to measure the heat evolution on firing explosives. A lighter form of bomb was constructed for him later, and used for fuels. Many other patterns have followed the original model.

In all bomb calorimeters oxygen is always employed at about 25 atmospheres' pressure. Further, no products escape during the experiment; and, since the combustion vessel is immersed almost completely in water, the whole of the heat is transferred for measurement. Calorimeters of this type are probably as perfect as possible, but their high cost has in the past allowed several inferior types to compete with them.

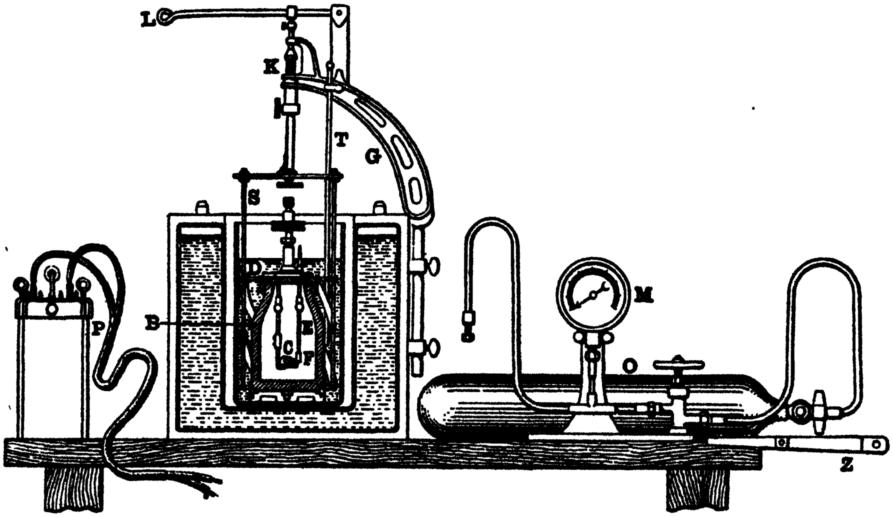

FIG. 72.—Mahler Bomb Calorimeter.

The application of the term "bomb" to calorimeters of the Parr sodium peroxide type is misleading.

The pattern chosen as illustrative of the "bomb" type is that of Mahler. The complete apparatus is depicted in Figure 72.

The bomb (B) is of steel, lined with an enamel to prevent corrosion. In some more expensive forms platinum or gold is employed, but an instrument with enamel lining will give satisfactory service. The cap screws on to the top of the bomb, and is made gas-tight by a suitable lead ring, the whole being screwed home by means of a large spanner whilst the bomb is gripped in the lead-lined clamp Z. At the centre of the cap an inlet valve for the oxygen is provided, and from the underside two platinum rods extend; one of these (E) is connected with a piece passing to the exterior, but electrically insulated from the metal of the cap, and the other carries the flat platinum capsule (C) in which the fuel is placed. A length of about 2 in. of fine platinum wire (0·0035 in. or 0·08 mm. diameter) is wound round the terminals of the rods, forming a loose loop which is in contact with the fuel. Alternatively the wire may be stretched tight and a loop of fine cotton tied round it and immersed in the fuel. Iron wire is sometimes recommended, but is best avoided; the oxide forms globules on the lining and quickly ruins it, and, moreover, entails a correction for its heat of combustion. In the long run, fine platinum wire is most economical.

The weight of fuel taken will vary with the type of calorimeter, because of their different water equivalents and weight of water used. The quantity used should ensure a rise of between 2½–3° C., to minimize errors due to thermometer reading. Solid fuels may be briquetted if desirable.

The charged bomb is immersed, as shown, in the water vessel of the calorimeter, being kept clear at the bottom by a perforated stand, into which it springs. There must be a free circulation of water right round the bomb. The calorimeter vessel is insulated from the capacious surrounding water vessel by a triangular wooden stand.

Oxygen is supplied from the cylinder O, which is connected by fine-bore copper tubing with a valve and the pressure gauge M. For filling, the bomb is attached at the top of the inlet valve to the end of the copper tube by a screw union.

The stirrer S is carried by the arm G, and operated by the lever L. Helical blades are provided on the stirrer, which moves up and down, and at the same time is given a rotary motion by the thread cut at K. Modern stirrers of the Archimedes screw pattern are more efficient. The battery for firing is shown at P; a two-cell accumulator is most convenient.

In operating, the firing wire should be arranged and always tested first with *one* cell, the two being used for firing. The fuel is weighed into the capsule, which is fixed in position by the small clamp on the rod. 10 ml. of distilled water are put in the bomb, it is then gripped in the clamp, and the cap carrying the capsule, etc., is screwed home carefully. Connection is now made to the oxygen pipe, the admission valve to the bomb opened two turns, and the manometer valve tightly closed. *Now* the valve in the oxygen cylinder is opened *fully*, and gas admitted by operating the pressure gauge valve, which is closed when 25 atmospheres is reached, the cap valve being then closed also.

It is important to operate the valves as described, and always to open the oxygen cylinder valve sufficiently. Cases of burst pressure gauges have occurred through neglect to have the manometer valve properly closed before the cylinder valve has been opened; also through partially opening the latter at the start, then, finding the pressure ceases to rise, opening out further so that the full pressure from the cylinder is thrown on the gauge. Hence, *always close the pressure gauge valve before making any alteration to the oxygen cylinder valve.*

The bomb being charged, attach the small stand, place centrally in the calorimeter vessel, into which the requisite quantity of water has been *weighed*, attach the stirrer, and see that all works smoothly, and that the stirrer will clear the thermometer. Finally, the thermometer is placed in position.

The water is stirred regularly, and the temperature noted every minute. It is a good plan to keep a large vessel of water in the room always, from which to fill the calorimeter vessel; then a constant temperature is reached very quickly. When the rate of rise, or a constant temperature, has been ascertained, attach one wire to the insulated pole, touch the top of the admission valve with the other wire, and fire the fuel. Stir regularly, noting the rise of temperature each half-minute, and continuing every minute for six or eight minutes after the maximum, to obtain data for the radiation correction. An accurate thermometer, reading to $\frac{1}{100}$th ° C. must be used; it should be tested by a competent authority such as the National Physical Laboratory to 0·002° if possible. The thermometer may be either of the Beckmann or the solid-stem type. If the former, calibration curves are necessary over several ranges of temperature to allow for variations in laboratory temperature. If a solid stem thermometer is used several must be available since the scale of such instruments is limited, and wider variations in laboratory temperature are to be expected. Zero variations in such thermometers are of no moment since it is the *rise* of temperature which is important.

A calorimeter should not be surrounded by a vessel with the object of preventing loss of heat—this is impossible—but it should be surrounded by a medium which makes the loss of heat regular in rate so that a correction can easily be applied. This condition is fulfilled best by a large mass of water.

The calorimeter described is advisedly the original Mahler type. The modern forms contain many improvements which cannot be entirely included by describing one proprietary form. The chief improvement is the use of rubber, in place of lead, washers whereby only a slight pressure is necessary to make the vessel gas-tight and failures are uncommon. The design of the joint is important since the rubber must be quite inaccessible to the flame. A second important change is the use of stainless steels, obviating the necessity for *platinum linings. Even stainless-steel bombs are best chromium-plated. Improvements in other details have been made so that the modern bomb is more easily handled than the old; it does not, however, necessarily give more accurate results.*

A section of modern bomb is shown in Figure 73, the B.T.L. bomb of Messrs. Baird & Tatlock, London, Ltd.

When a determination of the sulphur in the fuel has to be made the bomb should remain in the water vessel for not less than thirty minutes for complete absorption of the acid fumes by the 10 grams of water in the bomb.

After removal from the apparatus the valve is opened, the gases being allowed to escape. The bomb and cover and valve chamber are rinsed thoroughly with water, which is preserved when necessary for the estimation of the sulphuric and nitric acids formed.

With coals having a very fusible ash it is important to note that some carbon may be included in the fused residue. Huntley found the maximum error due to this equal to 3 per cent. on the calorific value. With a low ash content such error is generally negligible, but with a high ash of fusible character the possibility must not be overlooked. Coals and cokes which yield fusible ashes may require a thin layer of coarsely powdered quartz or asbestos in the bottom of the crucible, which prevents the inclusion of unburnt carbon in the fused globules, the quartz breaking up the larger fused globules.

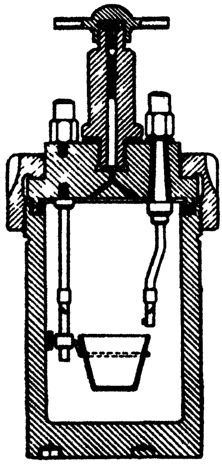

FIG. 73.—B.T.L. Bomb.

Occasionally hard fuels like anthracite and coke are difficult to burn; in such cases a small amount of highly combustible material of known calorific value, such as benzoic acid or hydrocarbon oil may be added.

Corrections required and calculation of the results. Combustible sulphur in the fuel burns to sulphur dioxide, which at the high pressures is oxidized further to sulphur trioxide, and this combining with water gives a further evolution of heat. As these two last exothermic actions do not occur with oxygen at normal pressures, a correction must be applied in accurate work. Further, nitrogen in the fuel and nitrogen in the residual air in the bomb form nitric acid at the high temperature reached and in the presence of water, heat being evolved again which must be corrected for.

The washings from the bomb must therefore be titrated to ascertain the total acidity (H_2SO_4 plus HNO_3).

The excess heat from the reaction $SO_2 + O + aqua$ is equal to 22·5 calories for each per cent. of sulphur.

The heat of formation of nitric acid per gram being 227 calories, for each ml. of $\frac{N}{10}HNO_3$ formed the correction is 1·43 calories.

To the washings from the bomb 50 ml. $\frac{N}{10}Na_2CO_3$ are added, the solution boiled down to 10 ml., diluted, filtered (from the ash and any lead sulphate which may have been formed) and washed. When cold the filtrate is titrated with $\frac{N}{10}HCl$ using methyl orange. The difference between these two titrations gives the total acidity (50 − T) and from this that due to H_2SO_4 (measured by direct precipitation as barium sulphate), must be subtracted to give the HNO_3 acidity (in terms of $\frac{N}{10}HNO_3$). Since 1 c.c. $\frac{N}{10}H_2SO_4$ is equivalent to 0·0016 grams of sulphur, this becomes

$$(50 - T) - \frac{\text{sulphur in wt. of coal}}{0{\cdot}0016} = n \text{ ml. N/10 nitric acid.}$$

The deductions in terms of calories to be made are then:

HNO_3 correction $n \times 1{\cdot}43$
H_2SO_4 „ S (per cent.) × 22·5

An alternative and simple method for routine work is based on the close agreement between the heat of formation of nitric acid per gram (227 calories) and the molecular weight of barium sulphate (233).

A solution of sodium carbonate containing 3·706 grams per litre is equivalent to 0·0044 grams of HNO_3 per ml., which means a correction of 1 calorie. Direct titration of the washings with such a solution, followed by filtration, washing, acidification with hydrochloric acid and precipitation of the sulphur as $BaSO_4$ will give the data for applying the following formulæ:

HNO_3 correction = ml. of standard Na_2CO_3 − 100 (wt. of $BaSO_4$)
H_2SO_4 „ = Percentage sulphur × 22·5

The magnitude of these corrections, and hence the importance of taking them into account, is shown by the following averages: nitric acid 15 calories, sulphuric acid 30 calories, a total of 0·6 per cent. on a coal of 7000 calories.

Cooling Correction. Elaborate systems of correction have been proposed, but for normal purposes one of these has been reduced to a form in which it can be applied conveniently by using a tabulated form. This is the Regnault-Pfaundler, the formula of which has the form (see B.S.S. 420, 1931):

$$\text{Correction} = nv + \frac{v' - v}{t' - t}\{\Sigma_1{}^{n-1}(t) + \tfrac{1}{2}(t_0 - t_n) - nt\}$$

$$= nv + k\text{T}$$

where n = number of minutes in chief period, usually 5.
v = rate of fall of temperature per minute in the preliminary period.
v' = rate in after period.
t, t' = average temperatures in preliminary and after periods.
$\Sigma_1{}^{n-1}(t)$ = sum of readings during chief period.
$\tfrac{1}{2}(t_0 + t_n)$ = mean of firing temp. t_0 and first temp. after which the rate of change is constant, t_n

and $k = \frac{v' - v}{t' - t}$ and is the "cooling constant" of the calorimeter and should be less than 0·0025.

Although the formula looks formidable the use of a blank form with spaces for the various readings makes its use as convenient and almost as rapid as that of the shorter methods. One shorter method is as given below in the form of an example. In this case the calorimeter had attained a constant temperature when the fuel was ignited.

Initial temperature (t_1), 15·52°.

Time after firing.	Thermometer reading.	Mean temperature of minute.	Mean difference from initial t.
1 minute	17·37	16·445	0·925
2 minutes	17·94	17·655	2·135
2½ "	17·95	17·945	2·425
3 "	17·95 (t_2)	17·945	2·425
4 "	17·945	—	—
5 "	17·935	—	—
10 "	17·860	—	—

Rise = 17·95 − 15·52 = 2·43

$$\text{Loss per minute} = \frac{17{\cdot}935\,[1] - 17{\cdot}860}{5} = 0{\cdot}015$$

Loss in 1st minute = 2·43 : 0·015 : : 0·925 = 0·006
" 2nd " = 2·43 : 0·015 : : 2·135 = 0·013
" 3rd " = 2·43 : 0·015 : : 2·425 = 0·015

Total correction . 0·034.
Corrected rise of temperature = 2·43 + 0·034 = 2·464°

[1] At the minute when the maximum temperature is reached and for the succeeding minute or two heat is still passing out from the bomb, more or less balancing the loss by radiation. To ascertain the true loss per minute by radiation alone, the temperature at which the rate becomes uniform must be taken.

The calorific value of the fuel is then calculated from the formula:

$$\text{calories} = \frac{(\text{T} + t) \times (\text{W} + w) - (\text{HNO}_3 \text{ correction} + \text{S correction})}{\text{weight of coal in grams}}$$

T = observed rise
t = radiation correction
W = weight of water
w = water equivalent

When fully charged with oxygen to the working pressure the bomb should contain not less than two and a half times the mass of gas, requisite for the complete combustion of the fuel.

The effect of lowering the initial oxygen pressure with a bomb calorimeter has been investigated by Allcut (*Eng.*, 1910, **90**, 755). With the sample of coal used the theoretical oxygen required was 1·33 grams per gram. The following results show the importance of working with at least 20 atmospheres initial pressure:

Pressure . . .	25	20·0	15·0	13·0	11·3	9·0	7·0	5·0	3·2
Weight of oxygen in bomb	19	15·2	11·4	9·94	8·64	6·9	5·41	3·92	2·42
Percentage of maximum calorific value	100	99·7	98·6	97·7	97·0	95·0	90·0	71·7	59·6

It is most important to note that, judged by the calorific value, at 3·2 atmospheres with nearly twice the theoretical oxygen the results are 40 per cent. below the truth. Unfortunately Allcut did not estimate the unburnt carbon, which at 13 atmospheres was first visible in the residue, neither were the products of combustion examined. The coal employed was anthracite—"because it was nearly pure carbon"—a bituminous coal would have given probably more complete combustion at the lower pressure.

Bomb Calorimeters. Very large numbers of tests have shown that the bomb calorimeter is the only form capable of giving consistent results with a reasonably high degree of accuracy. Adopting all corrections, Brame and Cowan found an experimental variation ranging from 0·16–0·30 per cent.; Gray and Robertson from 0·06–0·7 per cent. When small corrections are omitted the sum of these may amount to an error of 1 or 2 per cent., but it would be rare for them to be all in the same direction. For example, the omission of a radiation correction is counterbalanced largely by the omission of the nitric-sulphuric acid correction. With both these omitted, in the case of the five coals used by Brame and Cowan, the uncorrected value was about 50 calories (0·6 per cent.) below the fully corrected value.

The accuracy of the determinations of the calorific value of coal in the bomb calorimeter has been examined by Briscoe, Jones and Marson (Fuel Research Survey Paper 29, 1933), who find that the duplicate determinations should not normally differ by more than 90 B.Th.U. They make the probable error of one determination 25 B.Th.U. and state that the odds are 100 : 1 that a figure which represents the mean of two determinations will be within ± 67 B.Th.U. of the true value.

Determination of the Water Equivalent of Calorimeters

This determination must be made with every possible degree of accuracy for any type of calorimeter. Several methods may be em-

ployed, and it is desirable to employ more than one, to check the result. These methods may be:

1. Calculation from the weight and specific heat of the parts.
2. A practical determination of the specific heat.
3. By the combustion of substances of known calorific value.
4. By imparting heat to the system electrically, and finding the rise of temperature.

The first method can be only approximate; it is often impossible to ascertain the weight of the individual materials of construction, or to be certain of their specific heat. With a glass calorimeter vessel which is only partly filled with water, the proper allowance is impossible to compute.

The practical determination of the specific heat of the whole apparatus subject to rise of temperature is a most useful check and readily carried out.

The last two methods undoubtedly are the best, that of burning a substance of known calorific value being most convenient. The mean rise of three or four results should be taken, when the water value (x) will be found from:

$$\text{Calorific value of pure substance} = (\text{Weight of water} + x) \times \text{Rise of temperature}$$

Benzoic acid is recommended as the best material, its calorific value being 6324 15-degree cals. per gram. A little over one gram should be used.

The electrical method is capable of giving very exact results. C. J. Evans (*Eng.*, 1906, 82, 295) has described this method as applied to a Thomson-Rosenhain calorimeter. A heating coil was arranged in the place that a sample of fuel would occupy normally, connection with it being effected by means of a special insulated terminal and another on the body of the instrument, potential leads being connected just above those for current. The electrical quantities measured were current and potential, the former by a Weston ammeter, and the latter by Poggendorff's method of direct comparison with a Standard Clark Cell. Oxygen was supplied at about the same average rate as during a combustion.

The following data and method of calculation will make the procedure clear:

Duration of experiment = T = 600 seconds in both cases.
When W = watts

$$\text{Calories } (= \text{gram-degrees C.}) = \frac{WT}{4187} = 143{\cdot}3W$$

[J being $4{\cdot}186 \times 10^7$ at 15° C., which was the average temperature of the experiments.]

$$\text{Water equivalent grams} = \frac{\text{calories}}{\text{temperature rise }^\circ\text{C.}} = \frac{143{\cdot}3W}{\text{Degrees C}}$$

The necessary allowance must be made when the parts of the apparatus used in the determination are removed, this being calculated from their weight and specific heat.

The following figures are the results of experiments to determine the water equivalent on this system :

Temperature rise ° C.	Average watts.	Water equivalent grams.	
5·75	102·9	2564	2566
5·92	106·1	2568	

Calorimetry of Liquid Fuels

The calorific value of the heavier liquid fuels—all which do not give rise to an explosive mixture with oxygen—may be determined in a bomb calorimeter, and the general details are similar to those given above, with small variations in procedure to suit individual liquids.

Most liquid fuels may be directly weighed out into the fuel crucible and ignition effected by a cotton thread attached to the platinum ignition wire and dipping in the sample. The weight of the thread used must be ascertained and the heat resulting from its combustion deducted. The calorific value of thread is 4140 calories per gram.

If it is found that the fuel does not ignite and burn completely it may be absorbed in three or four paper discs or special cellulose blocks (weight being ascertained), but usually the absorption of the oil by a non-combustible material, kieselguhr, is preferable. With paper considerably less than the usual one gram of oil must be taken. The tray is half-filled with kieselguhr (previously ignited, as it always contains organic matter), the surface corrugated, the whole weighed, and the oil distributed over the kieselguhr and reweighed. More dry kieselguhr is then spread over the surface, and an almost " dry " oil-impregnated mass obtained. Some kieselguhrs are very fusible and are unsuitable for this use, for a considerable proportion of carbon may remain in the fused mass, which should be examined carefully at the conclusion of the experiment.

With very volatile liquids such as motor spirits, bomb calorimeters are dangerous and special precautions must be taken. During the time the initial temperature readings are being taken the spirit volatilizes and an explosive mixture forms which may detonate with violence. Another difficulty occurs in weighing spirits into the platinum crucible, losses by evaporation tending to give low results. Several expedients have been adopted in order to overcome both difficulties. These are (1) the covering of the crucible with a piece of thin rubber sheet, (2) the enclosing of the spirit in a glass bulb, and (3) the use of celluloid capsules.

The first expedient is satisfactory up to a point but is not too easy to achieve as the spirit vapour breaks the seal by dissolving the rubber. There is, however, no doubt about the correction figure for the weight of rubber used. The second is also successful about once in every two trials. There is *no* loss of weight if the bulb tip is broken only at the last moment, but the bulb seems to discharge its contents violently and some escape combustion. The last would be the most satisfactory if only capsules of uniform calorific value were obtainable; their variability unfortunately makes the correction for the heat of combustion of the capsule uncertain. A rather different expedient to guard against violent explosion is to add carbon dioxide to the oxygen; the addition of 20 per cent. is stated to give good results with cracked spirits.

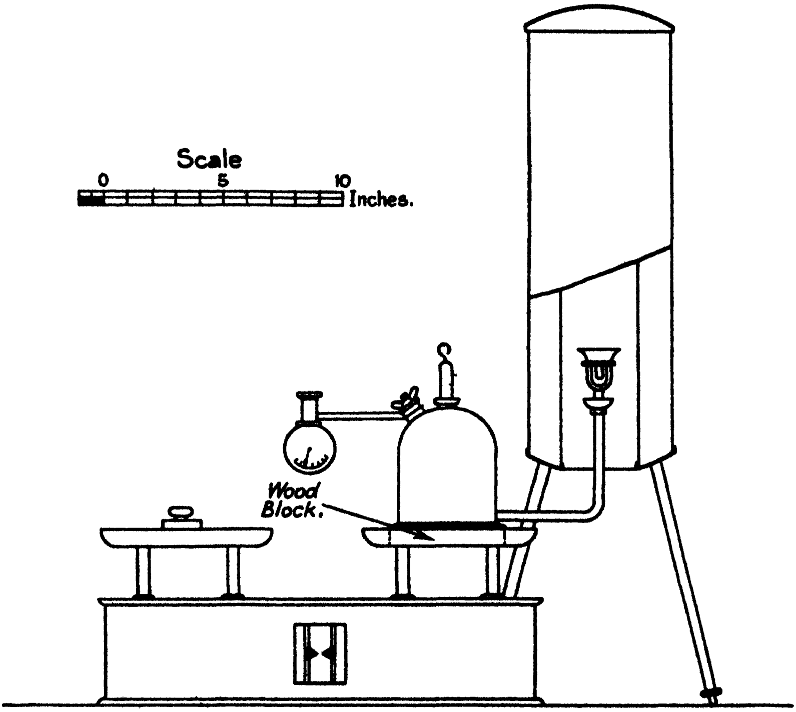

FIG. 74.—Gas Calorimeter adapted for Liquid Fuels.

An alternative method of obtaining the calorific value of spirits is to vaporize them and burn the vapour in a gas calorimeter. Watson (*J. Soc. Arts.*, 1910, 58, 990) used the method successfully, taking precautions to avoid selective evaporation of the spirit. For this purpose Immerkötter used a lamp of the Primus type. Other workers have used other lamps and suspended these in some cases (Harwood, *Eng.*, 1923, **116**, 396) from the arm of a special balance. One of the authors has used this method for many years but prefers a balance of the Beranger type, the arrangement being shown in Figure 74. At least 10 grammes of the fuel should be burned.

A volumetric method of measuring the fuel has been devised at the Fuel Research Station (Report of the Director, 1929, p. 67). In this apparatus a number of glass vessels in series, and arranged vertically, are connected to a burner. The bulb nearest the burner is filled with the fuel and the others with water. Mercury is delivered to the lowest bulb at a constant rate, displacing water and therefore spirit. The burner is constructed so that the fuel is vaporized as it passes the jet. The rates are so arranged that a Boys gas calorimeter can be used. The time over which combustion is measured is that during which the level of spirit passes two marks above and below the topmost bulb. The results are accurate to within ± 0·5 per cent., a small correction being necessary for CO in the products of combustion.

Calorimetry of Gases

The calorific value of a gas may be determined in a bomb, but so many calorimeters of a far more suitable type are available that the bomb is used but seldom. The small quantity of gas it is possible to employ is against the method.

The most suitable form of calorimeter is one with constant flow of water, and from the volume of gas burnt, the rise of temperature and weight of water heated, the calorific value is obtained at once.

The best known pattern is the *Junkers calorimeter*, which is employed almost exclusively on the Continent and in America, and very largely in this country. In the original pattern the thermometers for measuring the temperature of the inlet and outlet water were at great difference of level, which made reading inconvenient, and no ready means of directing the flow of water into the measuring vessel or to waste as required was furnished. In the latest pattern of the instrument these defects have been remedied and the design improved on in other respects.

The principle of construction is that the gas burns at a Bunsen burner in a central flue of sufficient diameter to ensure no impingement of the flame against the walls, the hot products of combustion pass to the top of the flue and then descend through small metal tubes arranged in a double circle around the central flue, finally making their exit near the bottom of the instrument. The water is supplied from a constant level tank and flows through the calorimeter in a reverse direction to the gas flow, consequently the exit gas should be cooled to the temperature of the inlet water. It is very necessary to provide proper admixture of the various streams of warm water;

this is accomplished by numerous baffles constituting a labyrinth below the exit thermometer.

The sectional diagram (Fig. 75), although of the older pattern, is most suitable to illustrate the construction and operation of this calorimeter. The hot gases rise to the top of the chamber, B, descend through the surrounding tubes, escaping at the lower flue, where a thermometer checks the temperature. The water is supplied to the constant level device, C, flows down D and passes through the quadrant control tap, E, past the inlet water thermometer, F. It escapes past the outlet thermometer, G, into the small tank, H, from which it flows through K to the measuring vessel, while a determination is being made, or alternatively to waste.

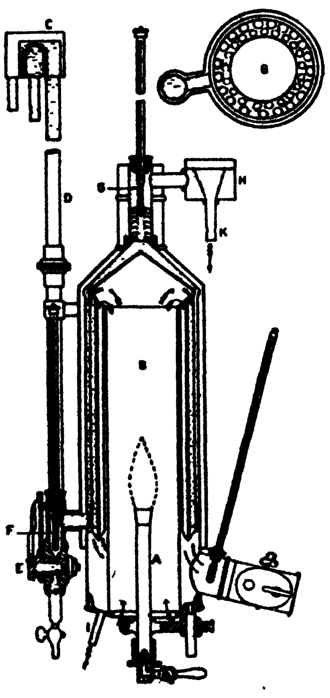

FIG. 75.—Junker Gas Calorimeter.

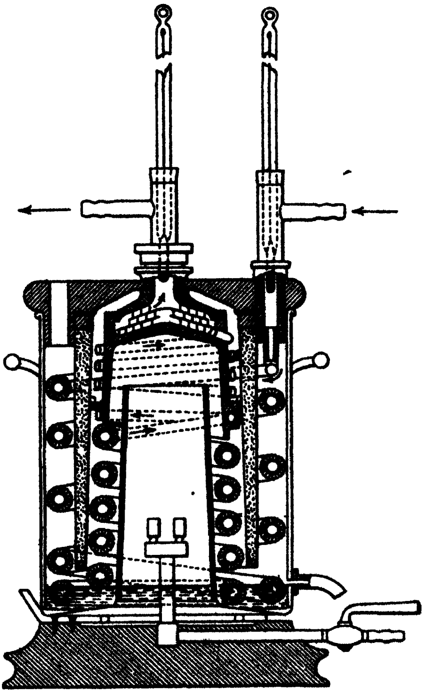

FIG. 76.—Boys Gas Calorimeter.

Water which is condensed from the products of combustion drains to the lower part of the instrument and escapes by the tube, I, under which a graduated receiver is placed. The water collected from a suitable volume of gas burnt furnishes data for the deduction from the gross calorific value when the net calorific is required also.

The *Boys calorimeter* was designed by Prof. C. V. Boys, one of the Gas Referees, at the time when official tests of the calorific power of the gas supply were introduced. Its essential features are that a very small volume of water is actually in the instrument at any one moment, the heat from the gases being abstracted by this water flowing through two spiral copper pipes in series, these being wound with wires, to increase their heat absorption. The instrument is compact, and when standing on a table both thermometers are at a convenient height for reading. The whole instrument may be lifted from the base, giving ready access to the burner, and the coil system may be lifted out attached to the wooden lid and the coils immersed in dilute alkali to prevent corrosion.

A section of the apparatus is shown in Figure 76.

The inlet water passes first through the outer coils downwards, then returns upwards through the interior coils, which are heat-insulated by a partition from the exterior coils, finally it flows around suitable channels on the exterior of the metal casting immediately above the chimney, and passes into a mixer with a labyrinth formed of coiled brass strips. Into the top of this chamber the outlet thermometer is fixed.

Two luminous flames from suitable jets are employed. The central chimney is always too hot for condensation of water to take place in it. At the commencement water is poured into the bottom of the vessel until it overflows at the spout provided. Proportionately condensation water flows from this spout during a run, and is collected and measured for the net calorific value determination.

With any type of flow calorimeter the equipment is completed by an accurate meter (one giving a complete revolution of the main index for $\frac{1}{10}$ of a cubic foot) and suitable pressure regulators. It is advisable to instal one regulator on the supply side of the meter and another between the meter and the instrument. The calorimeter should be fitted with a simple device for directing the water into the large measuring cylinder at the proper moment or to waste, without the operator being obliged to look away from the meter dial. In accurate work the temperature, and pressure at which the gas is supplied to the meter must be noted, and the volume passed corrected to saturated gas at 60° F. and 30 in. barometric pressure. It is very desirable that the water should be supplied at the temperature of the room, which may be arranged for by a supply tank, without ball valve, holding from 30 to 40 gallons.

In operating calorimeters of the flow type the adjustment of the gas and water supplies must be suited to the character of the gas. With coal gas about 6 cu. ft. per hour is suitable; poor power gases may be burnt at 3 to 4 times this rate. The water flow should be regulated so that the products of combustion should leave the instrument at as nearly as possible air temperature. In the Junkers calorimeter considerable control of this is possible by alteration of the damper in the exit flue. For the Boys calorimeter a correction of $\frac{1}{8}$ calorie for each degree difference in temperature between the exit gases and the air temperature must be added or subtracted from the results. In general, a difference in thermometer readings of 10° to 12° C. will give a suitable cooling of the exit gases.

A convenient quantity of coal gas to employ in a test is 0·3 cu. ft. The temperature of the inlet water thermometer should be read just before the test, as nearly as possible at the completion of the first and second revolutions of the meter, and immediately after the test. The exit water temperature should be noted at every quarter revolution; in each case the mean temperature from the observations is employed.

The main water supply must be adjusted so that a small quantity is always flowing to waste over the weir in the constant pressure device, and the calorimeter should always be run for from twenty to thirty minutes before taking a test, in order that conditions may become settled. When fresh water has been added to the meter or new rubber tubing employed, gas should be run through for some time in order to saturate them thoroughly.

Some small error is introduced by measuring the water instead of weighing it; in this country measuring is usual, in America the water is weighed. The simplest plan is to calibrate the measure for the weight of water around the average temperature at which it will be collected in practice.

With proper attention to these points the results will be accurate for all practical tests.[1] The thermal efficiency of a flow type calorimeter is about 99·5 per cent.

With a flow calorimeter the calorific value is obtained from the simple equation:

$$\text{Calories per cu. ft.} = \frac{\text{Weight of water in kilos} \times \text{difference of temp.}}{\text{Cu. ft. of gas at } 60^\circ \text{ F. and 30 in.}}$$

In an actual example—Temp. of gas 68° F.; barometer 29·7; water collected 3·945 kilos (litres); gas burnt 0·3 cu. ft. (= 0·297 at 60° F. and 30 in.); difference of temperature 11·6° C.

$$\textit{Gross} \text{ calories per cu. ft.} = \frac{3945 \times 11{\cdot}6}{0{\cdot}297} = 154{\cdot}0 \text{ (610 B.Th.U.)}$$

For the *net* calorific value it is desirable to burn at least 1 cu. ft. of gas and measure the quantity of condensed water (in ml.) collected from the drip pipe; calculate this to the amount obtainable per cu. ft. of gas. The amount of heat to be deducted from the *gross* value per cu. ft. will be obtained with sufficient accuracy by multiplying the number of ml. of condensed water per cu. ft. of gas by 0·6 Calorie.

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[1] The conditions affecting the accuracy of flow-type calorimeters have been fully investigated and the reader is referred to such standard works on calorimetry as Hyde and Mills, *Gas Calorimetry*, Ernest Benn, Ltd., 1932. The publications of the Gas Referees should also be studied.

Example. In experiment above, water collected from 2 cu. ft. of gas = 42 ml.

$$\text{Net value} = 154 - \left(\frac{42}{2} \times 0{\cdot}6\right) = 141{\cdot}4 \text{ Cals. (563 B.Th.U.)}$$

Still-water Calorimeters.[1] Where a regular supply of water is not available there are a number of calorimeters which can be operated with a fixed quantity of water. The first was that of Thomsen in which the gas is burned in a combustion chamber surrounded by water, the combustion gases passing through a spiral in the water. The water is stirred mechanically and the rise of temperature noted after a certain volume of gas is burned. Several modifications have been made to Thomsen's model by other investigators, but to-day none of them are used to any extent.

The Simmance-Abady portable calorimeter gives results which are correct only to about 3 per cent. A measured quantity of gas is burned in a calorimeter containing water such that its total heat capacity is equivalent to one litre. The temperature is read before and after and calorific value calculated using an instrument factor.

Instruments of a different type are explosion calorimeters, which are suitable for the examination of small quantities of gas. The best known are the Strache, Union and Löffler. In the Strache the heat produced by explosion is given to the air in a jacket round the explosion vessel. The increase of pressure of this air is taken as a measure of its calorific value. The Union is similar in principle, the air being replaced by an oil having a high coefficient of expansion. Blackie and Moss (*J. Sci. Inst.*, 1930, **7**, 84 : 1935, **12**, 188), after indicating certain necessary precautions, have shown that up to 750 B.Th.U. an accuracy of 0·5 per cent. is possible. This calorimeter has considerable value in laboratory work where only 100–200 ml. of gas are available. The Löffler calorimeter is really an improvement of the original Strache. A few ml. of gas are exploded in small pipette with a vacuum jacket and the rise of temperature observed. The results obtained do not seem so reliable as those of a calorimeter of the Union type.

RECORDING GAS CALORIMETERS

With the introduction of the Gas Regulation Acts the sale of gas on a " therm " value has necessitated the introduction of continuous recording calorimeters, the intermittent tests made with the usual type of gas calorimeter not fulfilling altogether what is required. Four such recording calorimeters have so far been approved by the Gas Referees, and these are described briefly below.

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[1] For further information see *Gas Calorimetry* by Hyde and Mills.

The records given by such instruments show the variation of the gas from a zero standard, such as the declared calorific value, and not the actual calorific value. The latter is determined by the Boys or similar flow type of instrument, and the readings on the chart of the recording instruments checked and assessed on these determinations.

Thomas Recording Gas Calorimeter. This instrument is of American design originally, but is manufactured in this country by the Cambridge Instrument Co., and has been certified by the Gas Referees for use in official testings. A full investigation of the accuracy of the instrument has been made at the Fuel Research Station and reference should be made to Fuel Research Technical Paper No. 20 (1928).

The principle on which the calorimeter works is the transfer of heat from the combustion of the gas to a stream of air and measuring the rise of temperature of this air. The products of combustion escape separately and at practically atmospheric temperature, the total or gross calorific value being automatically recorded. Since the gas, heat absorbing air and air for combustion are saturated before metering, and the gas and air are metered at the same temperature and pressure, results are automatically given for the gas at 30 in. and 60° F., saturated.

The calorimeter (Fig. 77) comprises the following:

1. A tank, in which a fixed water level is maintained by a chain pump and overflow weir.

2. Three meters within this tank; mounted in alignment and driven by an electric motor through gearing. These meters are respectively (*a*) the gas meter, (*b*) one for supplying the heat absorbing air, (*c*) one for supplying air for combustion.

The gear ratios require variation for gases of different calorific value, e.g. coal gas; water gas, etc.

3. The Burner Unit (Fig. 78). The burner tube and other parts exposed to the flame and hot products of combustion are of quartz. The gas from the meter mixes first with a stream of air from the combustion air meter, the mixture passing through a small orifice, to maintain a slight pressure in the chamber, so overcoming any slight irregularities in the rate of flow from the meters. A small amount of secondary air is supplied direct to the flame. The products of combustion pass downwards out of the burner, being cooled to within 2° or 3° F. of the temperature of the incoming air. The heat absorbing air passes separately around the burner tubes.

The burner casting is immersed in the water in the tank to within about 0·2 in. of its top, to ensure constant temperature conditions.

Before the test gas enters its meter it passes from the supply through a small orifice to a chamber open to the atmosphere through a "bleeder" burner, which prevents any pressure being built up. Approximately 3 cu. ft. of gas per hour is burnt at the bleeder burner, and a quarter of a cubic foot at the calorimeter burner proper.

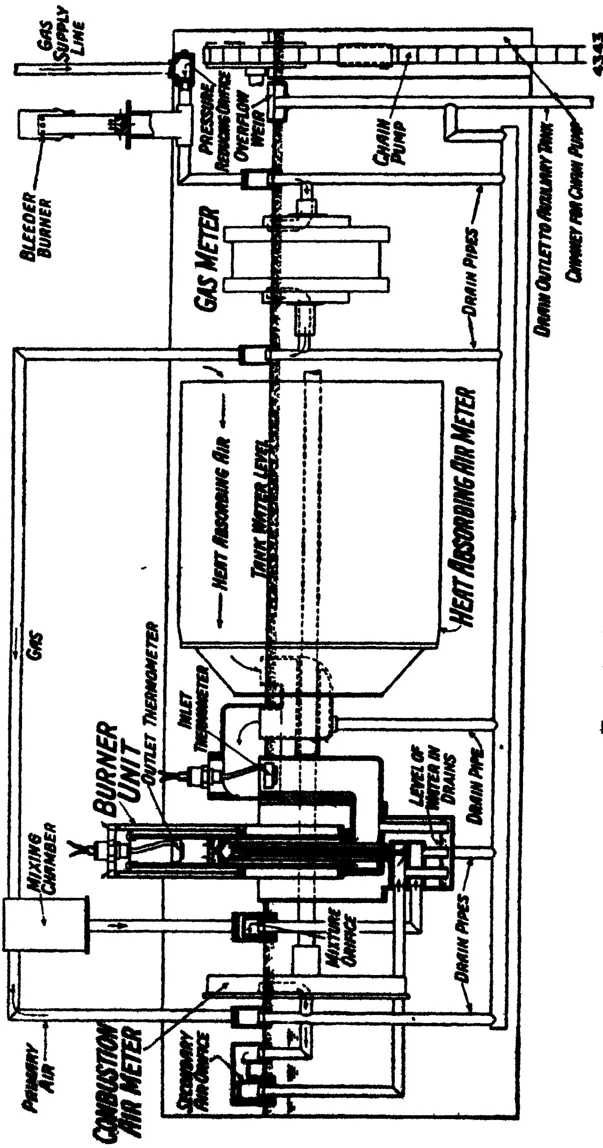

FIG. 77.—Thomas Gas Calorimeter.

4. The Thermometers. These are of the electric resistance type, with nickel wire. They are arranged respectively in the absorption air inlet and outlet, and are used differentially, forming two arms of

a Wheatstone bridge, the other two arms being fixed resistances incorporated in the recorder unit. The current for the bridge circuit is provided by a generator driven by the same motor which operates the meters.

5. The Recording Units. These may be fixed in any convenient position, near or away from the calorimeter unit. A continuous pen record is given on the chart paper, and an engraved scale above the pen enables a reading to be made at any moment.

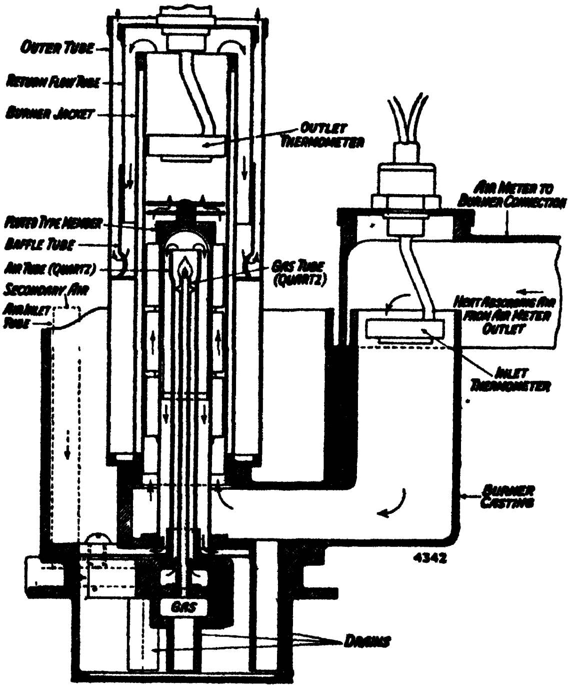

FIG. 78.—Burner of Thomas Gas Calorimeter.

The calorimeters are tested and adjusted with pure hydrogen, the gas delivery meter being run at such a speed that the temperature rise is equal to that which will be obtained with the gas for which the instrument will be used. On gases of steady calorific value in practice the calorimeter will record within ± 1 B.Th.U.

A description of the Boys and Sigma recording calorimeters by Kershaw will be found in *The Gas World*, 1932, 97, 317.

The Boys instrument is of the continuous water flow type, a measured quantity of water being heated by a measured quantity of gas, the differential temperature between the inflowing and outflowing water determining the greater expansion of amyl acetate in one sealed brass tube as compared with a similar tube. These brass tubes are 3 in. long and 2⅞ in. diameter and they are closed at each end by a corrugated brass or copper cap securely fastened on. By an ingenious lever system the slight movements of these diaphragms differentially is transferred to the pen of the recording chart. Water is supplied to the calorimeter from a tank with a constant level device, and then passes down through an air-cooled coiled metal pipe into a lower tank, from which it is raised again to the upper tank by a small pump. In this way a definite quantity of water is maintained in the outfit and the supply to the calorimeter is approximately at atmospheric temperature. The metering of the gas is automatically controlled to compensate for variation in temperature, pressure and humidity.

The Sigma instrument is based on a novel principle, the relative expansion of one of two long steel tubes, the inner one heated by the combustion of the gas, whilst the outer one is cooled by the incoming air. By a system of levers the differential movement is imparted to the pen of the chart.

The tubes are concentric, and are 17 in. long, firmly fixed together at the lower ends. Outside these there is a larger tube and the incoming air passes from the open top downwards to the flame, thus acting as a protection from loss of heat from the pair of inner tubes, and warming the air for combustion.

External governors provide in an ingenious way for the elimination of variables due to the temperature and specific gravity of the gas, or the temperature and pressure of the air. The governors are of the pressure type, two are fixed at the upper end of a vertical supply pipe, 6 ft. long. The first of these simply reduces the pressure of the entering gas to 2·5 in., thence the gas passes to the second governor, in which increase of pressure reduces the flow. At the bottom of the tube the governor there acts in the opposite manner, a rise of pressure opening the valve. The upper (second) governor is adjusted to give a pressure of 0·33 in. (water gauge), the lower to 0·25 in., the difference of 0·08 in. being the average difference of air pressure in the 6-ft. length of pipe. The pressure at the orifice of the supply tube is therefore proportional to the difference in weight of two equal columns of gas and air. The lower governor is connected by a flexible tube to the burner.

The Fairweather Recording Gas Calorimeter employs a Boys gas calorimeter which has been slightly modified to permit of its functioning as part of a recording instrument, yet allowing of its being used in the customary manner for individual check tests of the actual calorific value of the gas. The modifications comprise the use of either a differential air thermometer, with one bulb surrounded by the heated effluent water the other bulb being cold, since it is surrounded by the ingoing water, or, alternatively, differential electric resistance thermometers. If the gas is burnt at the rate of 5 cu. ft. per hour and exactly 6 litres of water are passed through the instrument for each cubic foot of gas burnt a definite rise of temperature of the water for gas of the standard calorific value is obtained and the record made by a recording pen operated by either the air or electric resistance thermometer will be on the datum line. Any variation on this will be recorded on either side of the datum line when the temperature difference between the inlet and outlet water alters due to change in the calorific value of the gas.

The principle is simple, but refinements are necessary in maintaining accuracy in measurement of the gas and controlling the water supply, for a definite flow of water must be ensured which is automatically adjusted to the temperature and pressure of the gas as metered. The rotation of the drum of the wet gas meter is controlled by either a pendulum escapement, or, in most recent patterns, by an electrically operated escapement. The gas is supplied to the meter through a cooler and saturator, so that it enters the meter at the temperature of the inlet water to the calorimeter.

CHAPTER XIX

SCIENTIFIC CONTROL OF THE PURCHASE OF FUEL AND OF ITS COMBUSTION

In spite of the enormous development of oil for steam raising and for use in internal combustion engines, the generation of steam is still the most important method of converting the heat energy of coal into work. The economy of the water-tube boiler in conjunction with turbines and the advances in the use of high pressure steam have falsified the view put forward with such confidence by some prophets that the steam engine would at an early date be relegated to the museums. Whilst under the best practice a boiler efficiency of 75–90 per cent. is attainable, by operating without some system of scientific control large but easily avoidable losses, which greatly reduce the efficiency, are incurred daily. Further, in the purchase of fuel for large plants very much better value for money can be attained almost invariably by applying common-sense rules.

From a consumer's point of view the value of a coal is dependent primarily upon its suitability to existing boiler-house conditions, and, secondly, on its calorific value. Its burning character, depending upon its freedom from excessive caking power, its average size, etc., will determine whether the requisite quantity can be burnt economically per square foot of grate area to give the steam required. Its calorific value is dependent upon the quantity of combustible matter actually present and the heating value of this combustible part.

Given that coals of a suitable character are available, it has been proved conclusively with various kinds of boilers that the practical value of coal for steam-raising is directly proportional to its calorific value as determined in some form of bomb calorimeter (i.e. gross value). Logically, it is as absurd to purchase coal without reference to its heating value as it would be for a metallurgist to pay at a uniform rate per ton for the ore of a precious metal without reference to the actual number of ounces of metal per ton of ore.

There has been naturally an adjustment of price to value; certain coals are so superior for steam-raising to others that they have commanded always a better figure. When such are employed the quality of deliveries is much better sustained when it is known that all deliveries are subjected to sampling and determination of calorific value. Where automatic stoking appliances are installed and control of combustion kept by the adoption of scientific methods, it often will be found that poor coal is quite suitable for use and in reality gives much better value for money than the special quality coals.

Whilst in some cases there is no option, if heavy freight charges are to be avoided, but to employ strictly local coals, it will be very exceptional to find no latitude of choice ; some coals are certain to give better value in heat units for a given price than others.

Purchase based on a guarantee of composition and calorific value never can be satisfactory with a natural product like coal ; it is so liable to variation in the quantity of combustible matter in different parts of the same seam, although the combustible matter has possibly a fairly uniform heating value, as to be against any guarantee. The simplest method, in cases where consumption does not justify the application of a full scientific system of purchase, will be that of contracting for the coal which, after trials of other deliveries of coals all suiting the conditions of practice, affords the greatest number of heat units per unit of cost, the penny being the most convenient unit of value. Comparison can be made on

$$\frac{\text{B.Th.U. per ton}}{\text{Cost in pence per ton}}$$

Should any deficiency in use become apparent, the calorific value determined on a properly-drawn sample will enable a comparison to be made with the original value on which it was decided to purchase this coal, and it would be possible to sustain a complaint, which with ordinary methods is next to impossible.

A factor which has operated in the past against the system has been the uncertainty of fair sampling and calorimetric determinations, on which payment must be based. In an article in the *Iron and Coal Trades Review*, August 18, 1911, the following results are quoted as obtained by three chemists or engineers for what purported to be the same sample —13,550, 14,050, and 15,360 B.Th.U. ! If results one-tenth as divergent as these are liable to be obtained, no one can accept purchase on a calorific value basis, and it is because figures have been put forward in the past showing enormous discrepancies that there has been a natural hesitation to be bound in the matter of a guarantee of heating value, or by a contract based on *pro rata* payments on the heat units of the fuel.

Purchase on a scientific basis can become general only when confidence is established in the accuracy of the tests, which, of course, involves fair and accurate sampling. Unfortunately the idea has been fostered that any untrained person can get the true calorific value of a fuel in some of the simpler calorimeters, an idea which, after many years' experience with most commercial calorimeters, the writers dispute unhesitatingly. For the same class of bituminous coal good comparative figures are obtainable, but the results can never have the degree of accuracy to serve as a basis for purchase; some form of bomb calorimeter in the hands of an experienced operator alone can furnish sufficiently trustworthy results.

The issue of standard methods of sampling and analysis under the authority of the British Standards Institution has now removed most of the objections which formerly could be urged logically against purchase on a scientific basis. It now remains to be seen how widely this will become used.

Two alternatives are open in arranging for the proper testing of the samples, presuming the specified directions for proper sampling have been certified as adopted. Three identical samples may be sealed up, one of these being examined for the consumer; if demanded, the other must be returned to the producer for his determinations, and a third preserved for reference to an independent expert, whose decision shall be final. On the other hand, as this might entail considerable expense, the parties may agree to accept the report of an independent authority in every case, on a certificate that sampling had been carried out exactly as specified, and with a provision for the independent expert to take his own sample if he considered it advisable.

Where contracts based primarily upon *pro rata* payments in accordance with calorific value have been running, it has been found invariably that the total economies resulting are much greater proportionately than the mere per cent. allowance. The United States Government are very large purchasers on this system, and their collected experience is that a saving of 20 per cent. is effected. Herein lies the great value of the system; not only is the price paid strictly proportional to the quality, but the knowledge that all deliveries are subject to constant sampling and determination of calorific value ensures that a much better average coal for steam-raising is supplied than under the old system.

Primarily then the price paid will be strictly proportional to the calorific value as delivered, a standard price per ton being arrived at in conjunction with the calorific value of the bulk sample submitted for trial. It is not desirable to make too fine a differentiation on the calorific value results or payments based on them in view of errors in calorimeter determinations in commercial practice possibly reaching half per cent., whilst with really good sampling a further error of the order of ± 1 per cent. is probable. Allowing a fair margin it would be reasonable to make 2 per cent. differences on the calorific value the usual practice, and this is the system adopted by the United States authorities.

The point has been raised whether the gross or net calorific value should be taken. The fallacy of regarding the latter as the true practical value has been dealt with already, but it is desirable to consider whether the net value is preferable as the basis. In the first place, the gross value is the one obtained in all calorimetric work with solid fuels, although one form of bomb calorimeter is said to be adapted for determining directly the water formed on combustion, but this must entail many difficulties which add greatly to the work involved. In practically every case the net calorific value can be arrived at only by a knowledge of the percentage of hydrogen in the fuel, and this again is ascertained accurately only by the tedious and generally unnecessary process of ultimate analysis.

Attempts have been made to calculate the hydrogen from the amount of volatile matter, but no satisfactory relationship has been established. It pre-supposes that the compounds yielding volatile constituents are similar in all cases, which is manifestly not the case. Excluding anthracites, which are not used for steam-raising, the extreme variation in hydrogen rarely exceeds 1·5 per cent., and in general with steam-raising coals is under 1 per cent. To obtain the net value the deduction for hydrogen required to be made from the gross value is 87 B.Th.U. per 1 per cent.; with 1·5 per cent. difference in hydrogen, this means a deduction of 130 B.Th.U., or about 1 per cent. on the heating value.

The difference between the gross value and the real practical value as compared with the difference between the net value and the same real practical value is, within the limits of variation in the amount of hydrogen found in coals, so nearly constant, certainly well within the combined limits of error of sampling and calorimetry, that the extra trouble involved in arriving at the net value is not commensurate with any slight gain. The gross value as determined by the bomb is all that is required.

Free moisture, however, demands very careful consideration. Heat will be expended in its evaporation and be lost through the steam produced escaping at flue gas temperatures. For the *net* calorific value of the sample as delivered a deduction would have to be made for this, but there are very good reasons for not taking this into account except in very abnormal circumstances. In the first place, the net calorific value is calculated always on the assumption that the products of combustion are at a temperature of 212° F., which is never the case, and this net value is no more the real available value than is the gross; it is only a little nearer the practical.

The heat involved for evaporation may be calculated from:

(*a*) Heat raising water from air temperature to 212° $(212 - t_1)$.

(*b*) Heat to convert to steam from and at 212° (967).

(*c*) Heat to raise steam from 212° to flue gas temperature (t_2). ($t_2 - 212$) × specific heat steam (0·48).

Then:

Weight of water per lb. of coal × $[(212 - t_1) + 967 + 0{\cdot}48(t_2 - 212)]$.

The magnitude of the values will be appreciated best by taking an actual example.

With coal: Ash 7·5 per cent. Calorific value on dry, 13,000; on combustible, 14,050: Air temperature, 60° F.; Flue gases at 500° F.

Moisture. per cent.	Calorific value on wet coal.	Additional B.Th.U. expended on evaporating moisture.	Percentage loss of calorific value.
5·0	12,350	62·5	0·50
7·5	12,025	93·7	0·78
10·0	11,700	125·0	1·06
12·5	11,375	156·2	1·37
15·0	11,050	187·5	1·70

The correction for heat expended in vaporizing this water to flue gas temperature will approximate in percentage lowering of calorific value to one-tenth only of the percentage of moisture. Hence, unless the delivery is exceptionally wet as compared with the standard coal, this additional factor hardly demands consideration. As further reasons for neglecting this there is the variation in the distribution of moisture throughout a large bulk of coal, for which it is not always possible to correct in sampling, and the fact that the coal as burnt is often much drier after storage than when delivered.

Moisture is throughout the most difficult point to deal with satisfactorily. In many cases it would be obviously unfair to saddle a contractor with penalties for what might be beyond his control, such as open trucks standing in the rain for some hours before unloading, but, of course, the converse is sometimes the case, and the sample is drier than on loading. Over a period it would in all probability give a balance if the sliding scale of payment was based on the calorific value of the dry coal, taking a certain determined percentage of water as normal, and therefore the standard, and making an additional allowance by calculating the actual delivery as so much per cent. above or below the quantity weighed in as the percentage of moisture is below or above the standard of moisture agreed upon.

The percentage of ash is another important item. Ash is allowed for *pro rata* with the reduction of calorific value, but above a certain amount ash is detrimental in far greater ratio than the actual percentage will show, and a *pro rata* deduction does not compensate the consumer properly when the ash is much above the standard.

There is additional trouble in the handling and disposal of ashes; if of a clinkering character it will be very troublesome; it leads to deposition of much dust in tubes and flues; it interferes with proper combustion on the grate, and it may be difficult to maintain the required output from the boilers. Above a certain amount then ash may well be subject to a penalty increasing more rapidly than the actual percentage increase, with right of rejection when a certain limit is exceeded.

The percentage of small coal again is sometimes taken into consideration, for if this is high it interferes with the proper air supply through the grate and larger carbon losses in the ash, etc., result. It is very difficult to make proper allowance for this in terms of money value, although some contracts include this.

Whilst the factors other than calorific value have been discussed in their relation to purchase on a scientific basis and are of importance, in the draft of contracts for what is largely an innovation on generations of practice, and of the fairness of which it is still necessary to convince many producers, the importance of simplicity in the terms cannot be over-rated. One would be disposed therefore to forgo many of these minor considerations for the great advantage to be gained by the general acceptance of the main principle of purchase *pro rata* on calorific value.

In developing any scheme of purchase based strictly on calorific value the primary object which should be kept in mind is that the consumer shall obtain regularly coal of the desired quality, and that the contract shall be so drawn that it is to the best financial interests of the producer to supply this quality. If below the standard the consumer shall not be called upon to pay more than a fair price, but, on the other hand, the producer must be assured of receiving what is fairly due to him should he supply coal honestly worth more than the standard price, and it is certainly to the interests of the consumer to obtain such fuel.

It is mainly because proposed contracts in this country have been drawn purely with a view of benefiting the consumer that very natural opposition has arisen to such a system of purchase on the part of the producer. If the latter can be shown that he is to be treated fairly, and that if he supplies coal of higher heating value than the average value taken as the basis of the contract he is going to obtain a higher price, in fact that the contract is perfectly equitable between both parties, this opposition will disappear.

When one of the authors first laid stress on the necessity for bonus as well as penalty clauses in contracts, Mr. G. C. Locket, then Chairman of the Coal Merchants Society, wrote:

"It is the first time in my experience that any one of authority has put forward the proposition that contract conditions should be perfectly equitable as between buyer and seller. Personally, I am disposed to favour the principle of selling fuel according to its calorific value, provided the method of sampling, the form of calorimeter used, the method of taking the analysis, and the adoption of a premium as well as a fine, is settled on a fair and equitable basis."

Although no "standard" coal specification is now in force, according to *The Iron and Coal Trades Review* (March, 1913), certain "standards" for washed and dry screened coals had been agreed on between some contractors and power station users, and formed the basis of some contracts. Two alternative specifications were drawn up, A for named coal, or coal of a particular description, B for coal guaranteed to have definite qualities as a fuel for steam-raising. The standards are given in Table LV.

TABLE LV

FORMER STANDARDS FOR GUARANTEED COALS

Washed Coals

Description.	Calorific value in B.Th.U.	Moisture	Small coal.
Durham and Yorks (bituminous):			
Double nuts	13,250	8	15·0 per cent. through $\frac{1}{4}$ in.[1]
Single "	13,000	9	17·5 " " $\frac{3}{8}$ "
Peas	12,750	10	20·0 " " $\frac{1}{4}$ "
Scottish (bituminous):			
Double nuts	12,750	10	15·0 " " $\frac{1}{2}$ "
Single "	12,500	11	20·0 " " $\frac{3}{8}$ "
Peas	12,000	13	20·0 " " $\frac{3}{16}$ "
Welsh (semi-bituminous and pseudo-anthracitic):			
Large nuts	14,300	5	15·0 " " $\frac{1}{2}$ "
Small "	13,900	6	20·0 " " $\frac{3}{8}$ "
Peas "	13,350	6	20·0 " " $\frac{3}{16}$ "
Dry Screened Coals.			
Durham and Yorks (bituminous):			
Double nuts	12,750	5	17·5 " " $\frac{1}{2}$ "
Single	12,500	6	25·0 " " $\frac{3}{4}$ "
Peas	12,250	6	25·0 " " $\frac{1}{4}$ "
Derby and Notts (bituminous)			
Double nuts	12,250	9	15·0 " " $\frac{1}{2}$ "
Double screened small nuts	12,000	9	20·0 " " $\frac{3}{8}$ "
Pea nuts	11,500	10	20·0 " " $\frac{3}{16}$ "
Leicester, Warwick and South Staffs:			
Double nuts	12,000	10	15·0 " " $\frac{1}{2}$ "
Double screened small nuts	11,750	10	20·0 " " — "
Pea nuts	11,250	12	20·0 " " $\frac{3}{16}$ "

[1] Sieves shall be square mesh with openings in the clear to the sizes given.

Payment under B was on a *pro rata* scale based on the calorific value with suitable modifications of the quantity paid for as delivered *according to the moisture and small* coal. No variation in the contract price *was made for variations in the calorific* value from the standard *not exceeding one-twentieth of the figures in the table.* The calorific value *was that determined on the coal after drying for 1 hour at* 104·4° C. (220° F.).

If the percentage of small coal were above (or below) the standard, the quantity weighed out was decreased (or increased) by a quarter of the percentage increase (or decrease) of small coal—percentage being taken on the bulk and not on the standard. If the moisture were less than 10 per cent. by weight, the quantity of coal to be paid for was increased beyond the quantity weighed in by a percentage equal to the percentage decrease of moisture. If the moisture exceeded 10 per cent. by weight, the weight of coal to be paid for was decreased below the quantity weighed in by a percentage equal to the percentage increase in moisture. Right of rejection of a consignment could be exercised if the moisture were more than 1½ times the standard or the proportion of small coal exceeded 25 per cent. by weight—taken on the bulk. The percentage of sulphur on the coal as received could not exceed 2 per cent.

The form of tender for coal for use in the London County Council Tramways Power Station lays down that the coal tendered may be of "the graded type, dry-cleaned or washed, suitable for mechanical stokers, or any smalls, dry-cleaned, washed or unwashed." The coal must be freshly wrought. If the coal is not of the class or kind contracted for it may be rejected, and if required the contractor must produce satisfactory evidence that it is the actual output of the colliery or seam from which it purports to have been obtained.

Amongst the particulars to be furnished are: (1) the calorific value (as received); (2) moisture; (3) volatile matter; (4) guaranteed ash and (5) percentage passing through a $\frac{3}{16}$-mesh sieve.

No *pro rata* allowances are included (as was the case at one time) for variation from a standard calorific value, it doubtless being considered that if the coal is specified as from a particular source, the calorific value of the coal substance (i.e. excluding the ash) will not vary materially.

The Council's standards of ash content are: (*a*) rough smalls or dross, 12 per cent.; (*b*) graded fuels, washed, 8 per cent. If the guaranteed percentage of ash be less than these figures, such less figure is to be used in the calculation of any allowance, but if the percentage of ash exceeds that stipulated (or the Council's standard for such coal, whichever is the less) the basic price per ton shall be reduced by 1*d.* per ton for every complete unit of such percentage excess up to 15 per cent., and 3*d.* per ton for each unit above 15 per cent. Conversely, if the ash is less the price will be increased 1*d.* per ton. Sampling and analysis is to be in accordance with the current recommendations of the British Standards Institution.

G. H. Tissenden, of the Cotton Spinners' Association, has recently discussed (*Industry Illustrated,* March 1933) the findings of his Company in connection with the purchase of coal on a calorific value basis. This company first started purchasing coal on a calorific basis in 1923, after some trouble in persuading the other contracting party to agree. Their findings are definitely in favour. Control is effected by the analysis of weekly samples collected as specified. When a new coal is being purchased the standard is adopted by agreement when the first month's analyses are available, with the saving clause of a review after an agreed period.

The variation in calorific value allowed on a coal of about 13,000 B.Th.U. per lb. (ash 10 per cent., moisture 5 per cent.) is ± 150 B.Th.U. A scheme of bonuses and penalties operates on the determined calorific values as follows :

(*a*) 13,151–13,321. Bonus 1*d.* per ton.
(*b*) 1*d.* per ton for each additional 60 B.Th.U.
(*c*) 12,791–12,850. Penalty 1*d.* per ton.
(*d*) 1*d.* per ton each reduction of 60 B.Th.U.
(*e*) A value of 1500 B.Th.U. below the standard of 13,000 means cancellation of the contract if it persists for two months.

If the percentage of ash exceeds 15 per cent. for two months the buyer may cancel the contract.

If the moisture content differs from 5 per cent. a bonus or a penalty again applies, if over 7·5 per cent. for two months the buyer may cancel.

4·01 to 6·00	per cent.,	standard price
3·51 to 4·00	,,	bonus 2*d.*
3·01 to 3·50	,,	,, 4*d.*
2·51 to 3·00	,,	,, 6*d.*
6·01 to 6·50	,,	penalty 2*d.*
6·51 to 7·00	,,	,, 4*d.*
7·01 to 7·50	,,	,, 6*d.*

The method of sampling under this contract is to take one spadeful from each cartful, collect these during one week in an air-tight box, break the bulk sample and reduce by coning and quartering and crushing to 2–3 lb. At the end of each month the weekly samples are well mixed and analysed by the buyer or his nominee and the seller. The former also seal a portion each month for reference. In case of dispute the matter is referred to the Testing House of the Manchester Chamber of Commerce, whose decision is final.

The methods of test in this otherwise excellent specification are not too satisfactory, but the fact that B.S.I. specifications are now available should soon remedy this.

Other clauses control the commercial conditions of sale.

CONTROL OF COMBUSTION THROUGH COMPOSITION OF FLUE GASES

The method of calculating the amount of air required theoretically for the combustion of fuel of given composition and the theoretical composition of the flue gases have been given in Chapter I, and data for such calculations in Table II, Appendix.

When the combustion of a fuel is complete the whole of the carbon should appear on the flue gases as carbon dioxide, accompanied by the nitrogen previously associated with the oxygen in the air. If this were attainable without excess air carbon dioxide and notrogen alone would constitute the flue gases. With excess air, as must be the case always with a solid or liquid fuel, free oxygen will be present in addition. On the other hand, when combustion is not complete carbon will be found in the flue gases partly as carbon monoxide and partly as hydrocarbons ; theoretically there should be no free oxygen under these conditions.

The efficiency of the combustion process is dependent upon two main factors :

1. Complete development of the maximum number of heat units of the fuel, attainable only by complete combustion.
2. Maximum utilization of these units, attainable only by avoiding all preventable waste.

The first condition is very important. All carbon appearing as the monoxide leads to serious loss, for 1 lb. of carbon then develops only 4,420 B.Th.U. per lb., instead of 14,650, as it does when burnt to carbon dioxide. Further, incomplete combustion of the volatile constituents (or products resulting from their decomposition by heat) leads to escape of hydrocarbon gases. From Table I, Appendix, it will be seen that such hydrocarbons have very high thermal values.

In general these losses through incomplete combustion can be avoided only by admission of a certain excess of air over that demanded theoretically, and necessarily this entails losses through sensible heat units carried by the flue gases, which up to a certain limit are unavoidable. For maximum practical efficiency a course must be steered clear on the one hand of the losses through incomplete combustion, without on the other hand running the risk of still bigger losses through unnecessary excess of air. Heat units must be sacrificed ; the important point is to adjust conditions of air supply so that this sacrifice is reduced to the minimum.

Assuming combustion were perfect with the theoretical air, heat would still be lost through the hot flue gases, the actual loss depending on the weight of the gases, their specific heat and temperature, or

$$m \times \text{Sp. ht.} (t_1 - t_2) = \text{B.Th.U.}$$

where m is the weight of gases per lb. of fuel, t_1 the temperature of the flue gases, t_2 the temperature of the air supply. Excess of air which must be allowed, as shown already, increases *m*, and the losses become proportionately large as $(t_1 - t_2)$ becomes greater. In addition to losses in the flue gases excess air causes direct cooling in the furnace, and reduces the efficiency of the heat transmission to the water.

It is clear then that the control of the amount of air actually employed in the combustion process is essential to good results, and consequently the means by which a proper judgment of the actual air supply can be ascertained must be considered carefully.

The determination of the proportion of carbon dioxide alone is a sufficiently good guide in general. Pure carbon on combustion with the theoretical air yields a volume of carbon dioxide equal to the volume of oxygen with which it combines ; hence, as air contains approximately 21 per cent. of oxygen, the gaseous products consist of 21 per cent. of carbon dioxide and 79 per cent. of nitrogen. For a fuel containing x per cent. carbon the flue gases will contain $\frac{21 \times x}{100} = y =$ carbon dioxide per cent.

The excess air with pure carbon will be found from

$$\left(\frac{21}{CO_2 \text{ found}} - 1\right)100.$$

For a fuel consisting of carbon only as the combustible together with non-combustible constituents, the excess air will equal $\left(\frac{y}{CO_2 \text{ found}} - 1\right)100$. In the case of a fuel containing hydrogen, a slight modification would be required, because the hydrogen burns with oxygen, forming water, which is condensed, and the carbon dioxide is estimated always in the gases after this condensation ; but for practical purposes this may be neglected, and the last formula applied as giving a sufficiently accurate approximation. It is not possible, however, always to obtain the composition of the coal from which y is calculated, but, taking coals generally, the amount of carbon dioxide present in the flue gases with theoretical air supply will lie between 18·5 and 19 per cent. On the basis then of $\left(\frac{18{\cdot}5}{CO_2 \text{ found}} - 1\right)100$, the excess of air may be ascertained approximately, and for a given heating value of the coal and flue gas temperature the loss of heat units for different excess quantities of air calculated. In the diagram (Fig. 79) curves for a typical case are given for three different flue gas temperatures.

It will be seen that the rate of increase of loss through excess air down to 12 per cent. of carbon dioxide is not great, but below this figure the losses may increase rapidly. In an attempt to work with too high a carbon dioxide figure great risk is run of incurring far more serious losses through incomplete combustion, and a safe maximum for carbon dioxide may well be fixed at 14 per cent. for coal on grates and somewhat higher for powdered coal or oil.

The combustion engineer would always be well advised to construct curves for the fuels he normally deals with in order that he can apply observed data to them rapidly and avoid repeated calculation. Charts have been constructed for this purpose covering coals over a range of carbon and hydrogen percentages, and their use is strongly to be recommended. If the composition (C and H) of a fuel is known (even approximately), and the composition of the flue gas, the owner of such a chart can read off the amount of excess air he is using and extent of his heat losses due to incomplete combustion or as sensible heat in his flue gases. One nomogram of this type is to be found in *Technical Data on Fuels* (*loc. cit.*).

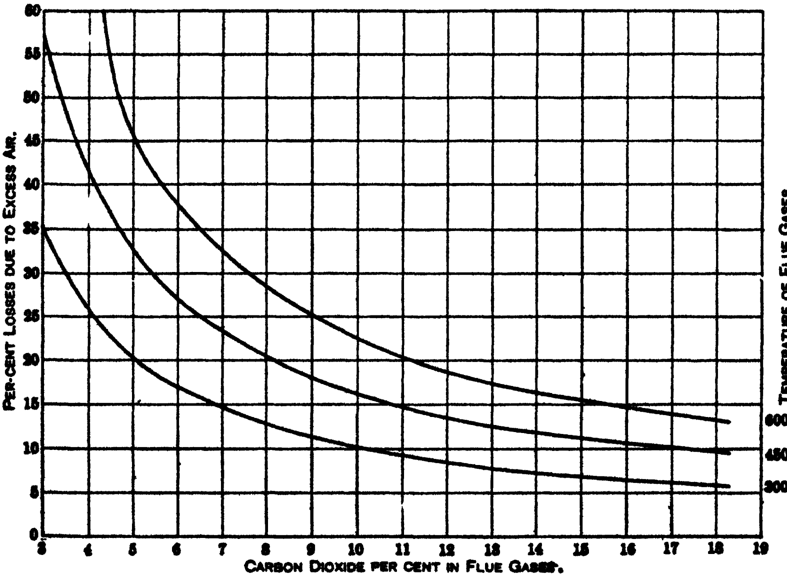

Fig. 79.—Loss of Heat in Flue Gases at Different CO_2 Percentages.

Calculated for a steam coal, 87·0 per cent. carbon; 4·5 per cent. hydrogen; assuming a mean specific heat for the flue gases of 0·24; 18·3 per cent. CO_2 in flue gases correspond with 11·6 lb. of air theoretically required.

The degree of incompleteness of combustion is usually measured by the amount of carbon monoxide present in the flue gas. The amount of excess air necessary to prevent incomplete combustion depends upon the fuel burned and the type of furnace. Almost complete combustion with little more than theoretical air can be obtained with gas and oil firing and with pulverized coal. With grate firing of coal or coke this is not possible, and even 100 per cent. excess air does not eliminate

CO from the flue gases. It is generally conceded that a compromise between heat losses by incomplete combustion and as sensible heat in the flue gas is obtainable with about 25 per cent. of excess air (see U.S. Bur. Mines Bulls. 135 and 137 and Tech. Paper 139).

Several simple forms of apparatus are available for the rapid determination of carbon dioxide in flue gases, and the application of these is often a valuable guide, but conditions during operation of a boiler plant, especially with hand-firing, vary so from time to time that these intermittent tests have nothing like the value which a continuous recording apparatus has.

Analysis of the flue gases by one of the well-known methods enables not only the CO_2 to be determined, but also the carbon monoxide and oxygen. From the results a good knowledge of the conditions may be derived, but such determinations take some time and involve the collection of samples at fairly long intervals. The Orsat apparatus is the one in most general use.

Continuous indicators and recorders (many so called are really intermittent, drawing the sample at every four to five minutes) for the CO_2 content give all the information requisite, except in special cases. Some, however, have been adapted to give a record of the carbon monoxide content of the gases. CO_2 recorders may be classified as (*a*) chemical, (*b*) physical. The former depend upon the measurement of a definite volume of the gas, the absorption of the CO_2 by strong caustic soda (NaOH) or potash (KOH) solutions, or by specially prepared slaked lime, the diminution in volume being automatically registered. Physical methods include measurement of the density of the gases compared with air, flue gases being about 8 per cent. heavier, and methods based on the relative heat conductivity of the gases involved.

Some of the earlier apparatus employing caustic alkalies were by no means simple in construction and included complicated glass parts, with many rubber tubing connections. Their maintenance in working condition required skilled and daily attention, and it was not uncommon to find that where this had not been given they had fallen into disuse. Caustic alkalies in strong solution are also very unpleasant to handle, and may easily be the cause of accidents.

An absorption instrument in which fine slaked lime was the absorbent was the Bi-Meter CO_2 Recorder. This instrument was originally designed by Bayer, and its operation will be followed from the diagram, Figure 80. The amount of carbon dioxide was recorded by two gas meters, which measured the gas before and after absorption of the carbon dioxide. Consequently the meters revolved at a different speed, and by means of suitable gearing operated the pen on the recording drum. There were no glass parts to get broken and no rubber tubing to perish.

As shown in the diagram, the gases were drawn first through a soot filter, which contained wood shavings and wood wool, the inverted bell standing in a water seal. From the filter the clean gases passed through a water-cooled system, the " temperature equalizer," and then on to the first meter. The carbon dioxide was absorbed in the large absorption chamber, in which layers of fine slaked lime were placed, these being separated by alternate layers of wood shavings ; the lime required renewal every third day.

The heat of reaction rendered the gas warm, so it passed through a second temperature equalizer, and then through the second meter, finally going through the aspirator and to waste.

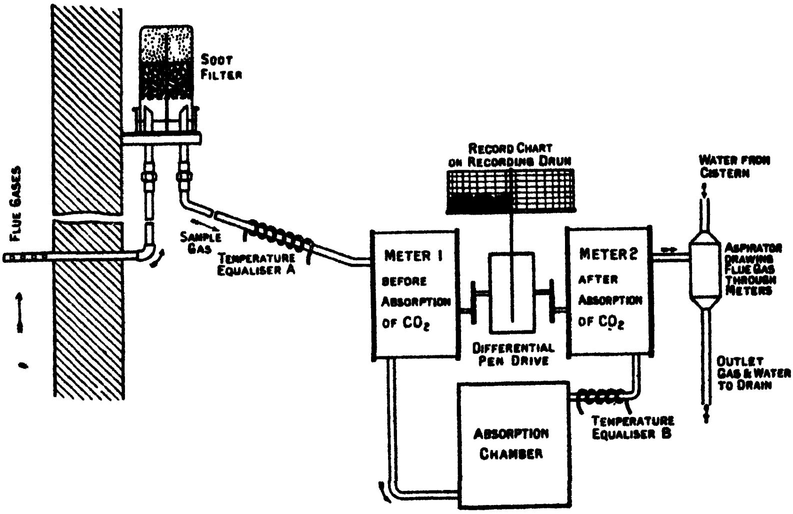
Soot Filter
Record Chart on Recording Drum
Water from Cistern
Flue Gases
Sample Gas
Temperature Equaliser A
Meter 1 before Absorption of CO_2
Meter 2 after Absorption of CO_2
Aspirator drawing Flue Gas through Meters
Differential Pen Drive
Outlet Gas & Water to Drain
Temperature Equaliser B
Absorption Chamber

Fig. 80.—Bi-meter CO_2 Recorder—Diagram.

Whilst the diagram shows very clearly the principle of working, it does not indicate the compactness of the apparatus. The temperature equalizers were arranged, of course, in one vessel, a long cylindrical vessel on the right-hand side of the case ; from here the water passed to the aspirator. The absorption chamber was arranged in the lower part of the case. The fluid in the meters was oil, and the level in each was so adjusted that with meter 2 running 4 per cent. slower than No. 1, both working on air, the line ruled by the pen just reached the zero line on the chart. When carbon dioxide was being absorbed the speed of meter 2 was reduced further, the pen marking the corresponding percentage of carbon dioxide.

Compound recorders measuring both oxides of carbon operate on the principle of removal of CO_2 by caustic solution, combustion of the CO in the residue in a tube containing copper oxide heated to a red heat, and final absorption of the CO_2 formed. The chart shows a double record for CO_2 on the one hand and theoretically $CO + CO_2$ on the other. The difference is an excellent indication of incomplete combustion but is not an exact measure of it owing to the possible presence of hydrogen and hydrocarbons in the flue gas. The "Mono" is a well-known instrument of this type.

Physical Methods. Although in the early forms physical methods were not very trustworthy, improvements have now led to their largely replacing the chemical methods.

The difference in density of flue gases and air was employed in some form of gas balance. Average flue gas is about 8 per cent. heavier than air, but as one litre of air weighs only 1·29 grams, the weight difference for flue gas is only of the order of 0·1 gram, and direct weighing consequently was liable to give very approximate results. Methods for improvement include the rate of passage of the gases through capillary tubes or, as in the Ranarex instrument, magnifying the small density difference by impelling air and the flue gases, with a powerful swirl, by fans attached to the shafts of two independent electric motors against two other fans with flat vanes. The air and gases being impelled with opposite rotary motions, the difference of torque of the two shafts enables a system of levers to be coupled to the respective ends of the shafts of the energy absorbing vanes and so operate an indicating pointer and trace a record on a wax paper chart. The impelling motors have a speed of 3000 r.p.m. If there is a slight difference of speed this is readily compensated for by a small adjustment of the zero.

Since water vapour will affect the density, it is necessary to bring both the air and flue gases to the same state of humidity-saturation. This is arranged for by humidifiers through which the gases pass.

The Ranarex instrument has been used for the measurement of small differences of density of gases at the Fuel Research Station and further details will be found in Technical Paper No. 5 (1922) and in a paper by A. Blackie and B. H. Williams (*Jour. Scientific Instruments*, 1929, **6**, No. 5, p. 157). It was found that small differences of density of two gases could be determined with a considerable degree of accuracy. Its rapidity of action enabled it to be used for this purpose where rapid changes had to be studied and other apparatus was inadmissible.

Electrical Recorders. These are based upon the principle that if a wire of a non-oxidizable metal, like platinum, be heated by a steady current in a closed space, the actual temperature it attains is determined by the heat conductivity of the surrounding gas, provided that the convection and "end losses" are reduced to a negligible amount.

If the conductivity for heat of air is taken as unity, the conductivity of hydrogen is 7, whilst that of CO_2 is 0·59. The actual temperature attained then by one of two wires through which the same current is passing will, if the wire is surrounded by air, be considerably lower than in a wire surrounded by gases containing carbon dioxide. On the other hand, it must be noted that as hydrogen has seven times the conductivity of air, a small percentage in the flue gases will tend to make the difference of temperature due to CO_2 less.

An instrument based on these principles was designed by Siemens as early as 1908, and G. A. Shakespear is responsible for the instrument described below, now made by the Cambridge Instrument Co.

This comprises (*a*) the soot filter (necessary with all recorders), (*b*) the CO_2 metering unit, (*c*) indicating and/or recording instruments, connected to (*b*) by suitable lengths of insulating leads.

The arrangement of the metering unit is illustrated by the diagram (Fig. 81) and the vertical section (Fig. 82). Four identical spirals of platinum wire are enclosed in separate cells, E_1–E_4 (Fig. 81), in a metal block, each forming an arm of a Wheatstone bridge. When two gases of different thermal conductivity are introduced, one into the pair of cells, E_1, E_3, and the other gas into E_2, E_4, the respective wires in these will cool at a different rate and maintain a different temperature. The difference of resistance will throw the Wheatstone bridge out of balance and the galvanometer, G, will be deflected to a degree which depends primarily on the difference of conductivity of the two gases. It is arranged that changes in temperature of the gases affect both sides of the bridge equally. If the cells E_2, E_4, contain air, and the cells E_1, E_3, flue gas, the extent of deflection will indicate the amount of CO_2 present, the galvanometer being calibrated to show the percentage. Carbon monoxide, nitrogen and oxygen have so nearly the thermal conductivity of air that small variations in these accompanying gases have no appreciable influence on the results. Hydrogen, however, as already mentioned, may have an influence.

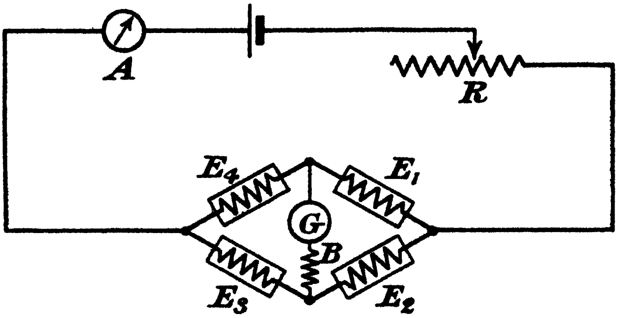

FIG. 81.—Electrical Arrangement of Cambridge CO_2 Recorder.

The current in the Wheatstone bridge circuit, as shown by the ammeter, A, is adjusted to a constant amount by the rheostat, R, whilst the resistance, B, in the galvanometer circuit enables the electrical zero of the CO_2 meter being adjusted.

A diagrammatic section of the metering unit as assembled is shown in Figure 82. The four cells containing the platinum spirals are arranged in the upper part, A, of the gun-metal block, K, the lower part comprising the bubbler, F, and aspirator. The gases pass first through the water and then through the annular surface cooler, G, to the meter and thence to the central pipe, H, which forms the aspirator. The meter block, A, is water cooled by the jacket, J, in which the annular cooler, G, is also immersed. The two air cells are sealed, but provision is made to keep the air at saturation by means of a moist wick. Current may be taken from the electric supply mains or be provided by an accumulator.

The same principle is adopted in what is known as the carbon monoxide metering unit, although this really records approximately the percentage of combustible gases in the flue gas. One pair of cells pass the flue gas directly; from them the gases then pass through an electrically heated furnace. In this the carbon monoxide is converted to CO_2, methane to CO_2 and water, and the hydrogen to water. The cooled converted gases then pass through the other pair of cells, when the increase in CO_2 will be measured.

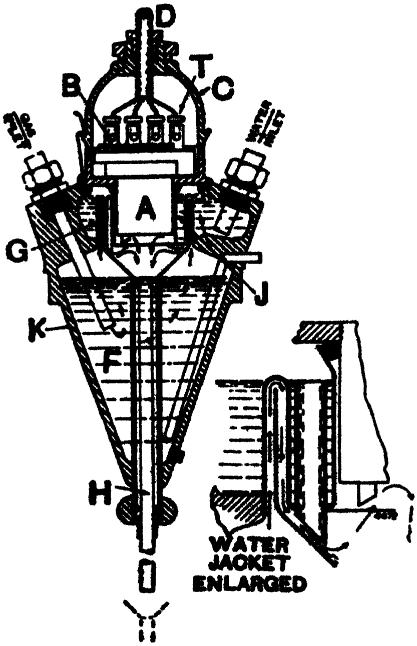

Fig. 82.—
Section of Cambridge CO_2 Recorder.

It is claimed for the electrical type that the operating costs are very small, that little attention is required compared with the chemical type, and that the gases are continuously under examination, intermittent samples and subsequent absorption of the CO_2 being avoided.

It is claimed further that results are accurate to within 1 per cent. of the carbon dioxide and monoxide content, but with the latter, under reasonable furnace conditions, the amount present should be quite small.

It must be emphasized that carbon dioxide alone furnishes the easiest and most applicable method of estimating excess air, but that carbon dioxide is only a measure of the heat losses due to this *when it is not accompanied by carbon monoxide.* A further small error is intro-

duced by sulphur dioxide, produced from combustible sulphur in the fuel. This gas is absorbed also by the reagents which absorb carbon dioxide.

The saving of fuel when recorders have been installed generally has been very considerable. In many cases they have revealed that not more than 5 per cent. of carbon dioxide had been obtained in ordinary working before this check was introduced. With the instruments fitted in a suitable position, the record is at all times visible to the stokers, who are found usually to take a proper interest in maintaining the standard of the flue gases, and as a check to excessive firing at infrequent intervals during the night shifts they have proved of great value. In power stations with widely varying load it is difficult to obtain proper adjustment of conditions for the best results without the employment of some such system, and as a means of detecting irregularity in the working of automatic stokers they are valuable.

A word of caution is necessary in reference to air leaks through boiler settings, etc. This would lead to low carbon dioxide, and the cause would be detected by failure of reduction of the air supply to the furnace to raise the carbon dioxide. There is, however, the risk that in attempting to do this, in the absence of knowledge as to an air intake, losses through incomplete combustion might be incurred.

In the operation of producer gas plants the automatic carbon dioxide recorders prove of value in controlling the working conditions, as the carbon dioxide is a most useful indication of the reactions taking place.

Automatic recorders, especially those of the chemical type, require regular attention if they are to be kept operating satisfactorily, but this attention, if regular, need occupy but little time. Particular attention must be directed to the cleansing of the gases by a suitable soot filter, which should be readily accessible for cleaning and renewal of material, and to arranging the gas pipes so that water does not condense and collect in bends: drain cocks should be provided at such points. The pipe system should be blown through at frequent intervals with compressed air or steam. With attention to the recorders as part of the daily routine of the boiler-house the instruments are capable of invaluable service, but with neglect for some days so much requires doing that it is never attempted.

FUEL CONSUMPTIONS

Fuel Consumptions. A vast amount of information on the consumption of fuel is scattered throughout the literature dealing with power production. It is impossible to convert the whole of the heat energy of the fuel into useful work, and the proportion which can be converted, even under the best conditions, varies over a wide range for plant of different type. This proportionate conversion of heat into work is expressed as the "efficiency" of the plant. The over-all efficiency includes that of the boiler and steam engine, or, in the case of gaseous fuels, of the producer and gas engine. In the case of the steam plant the efficiency of the boiler will vary with the type, but for any type will depend very largely on the proper control of the combustion process, a subject discussed at length in the preceding chapter. The consumption per H.P. generated is lowest the nearer the plant is working to the maximum output.

In order to give a general comparison of the relative value for power of the various fuels already dealt with in previous chapters, Table LVI has been arranged, based upon the theoretical horse-power obtainable in a perfect heat engine. Since 1 H.P. is equal to 33,000 ft.-lb. per minute, the H.P.-hour is equivalent to 33,000 × 60 = 1,980,000 ft.-lb. The B.Th.U. is equivalent to 778 ft.-lb. Hence with the perfect heat engine

$$\text{B.Th.U. per H.P.-hour} = \frac{1{,}980{,}000}{778} = 2560.$$

TABLE LVI

COMPARATIVE CONSUMPTION OF FUELS AT VARIOUS THERMAL EFFICIENCIES

(*Based on the perfect heat engine requiring* 2560 *B.Th.U. per H.P.*)

Thermal efficiency per cent.	Type of engine of this efficiency.	Equivalent in B.Th.U. required per H.P.	Quantity of different fuels to provide these units.				
			Coal. 12,500 B.Th.U. per lb.	Oil and petrol. 19,000 B.Th.U. per lb.	Coal gas. 600 B.Th.U. per cu. ft.	Producer gas. 140 B.Th.U. per cu. ft.	Blast furnace gas. 90 B.Th.U. per cu. ft.
40	Diesel engines . .	6,400	0·512	**0·336**	10·4	45·7	57·5
35		7,320	0·586	**0·385**	12·2	47·0	81·3
30	Large gas engines .	8,530	0·683	0·450	14·2	**61·0**	**94·8**
25		10,240	**0·819** (*a*)	**0·540**	**17·0**	**3·2**	**114·0**
20	Gas engines, ordinary oil and petrol motors	12,800	1·024	**0·675**	21·6	91·4	142·5
18	Large turbine sets, over-type superheated steam	14,200	**1·136**	0·75	23·7	101·0	156·0
15	Small turbine sets, high-speed reciprocating condensing .	17,050	**1·365**	0·90	28·4	122·0	189·5
10·0	Ordinary expansion condensing . . .	25,600	**2·08**	1·35	42·7	183·0	285·0
7·5		34,200	**2·73**	1·80	57·0	244·0	380·0
5·0	Small reciprocating non-condensing	51,200	**4·10**	2·59	85·4	366·0	570·0

NOTE.—Figures in heavier type indicate the usual fuel and the average consumption.

(*a*) When gasified in producers.

Considerable differences in thermal efficiencies, and therefore in fuel consumptions, are met with in practice, and although in some cases higher efficiencies are met with in special test runs, those given in Table LVI afford a fair guide under good running conditions.

Sankey (*J. Roy. Soc. Arts*, **110**, 3127, p. 1089) gave the data reproduced in Table LVII for the fuel consumption in various types of plants at varying loads.

TABLE LVII

Fuel Consumptions at Various Loads

Description of plant.	Calorific value of fuel B.Th.U. per lb.	Total fuel required—lb. per hour at various proportions of full load.				
		Quarter load 25.	Half load 50.	Full load 100 B.H.P.	10 per cent. Over-load 110.	50 per cent. Over-load 150.
Non-condensing steam plant	13,000	150 200	190 240	270 320	290 340	— 410
Condensing steam plant	13,000	95	120	190	210	310
Overtype superheated condensing steam plant	13,000	55	75	130	150	230
Gas engine, pressure producer	13,000	37 53	57 70	93 104	— 110	— 140
Gas engine, suction producer	14,000	34 49	53 64	85 96	— 104	— 130
Oil engine	19,000	26 33	40 46	65 72	— 78	— 97
Diesel engine	18,500	16 19	25 27	45 45	51 50	— 69

Where two sets of figures are given for the same class of engine, the upper is for 100 H.P. plant, the lower for 150 H.P.

Under ordinary conditions in practice the figures in Table LVIII have been deduced from a large number of records. The over-all efficiency in the case of steam plants includes boilers and engines; in the case of gas plants it includes the producer, cleansing plant, and engine efficiency. Of course, the consumption per B.H.P.-hour is greater for small power engines, but with internal combustion engines the increase is very much less than with steam plant.

Complete records of fuel consumptions in the electric generating stations of the country are published in the Annual Return of Fuel Consumptions and Units Generated (*H.M. Stationery Office*). In 1932 the highest thermal efficiency in a steam (turbine) generating station was 24·72 per cent. Many Diesel engined stations had a thermal efficiency of some 29 per cent.

TABLE LVIII

Over-all Consumption of Fuel per B.H.P. at Full Load under Running Conditions

Steam Plants

Type of engine.	Approx. overall efficiency.	Lb. of fuel. Coal.	Lb. of fuel. Oil fuel.
Small reciprocating non-condensing	5	4–5	—
Large multiple expansion condensing	6–7	3–4	2–2·5
Small turbine sets and over-type superheat condensing	12–15	1·4–1·7	0·9–1·1
Large turbine sets	18	1·3	0·75

Gas Plants, Town gas; Blast furnace gas.

		Lb. of fuel in generator.	Cu. ft. of gas.
Pressure producers	20	0·9–1·1	80–90
Suction producers	22	0·8–1·0	80–90
Town gas	25–27	—	16–18
Coke oven gas	25–27	—	20–21
Blast furnace gas	25–27	—	100–110

Oil Engines.

		Nature of fuel and sp. gr.	Lb.	Pints.
Petrol motor	18–22	Petrol (0·722)	0·63	0·7
Ordinary oil engines	18–25	Kerosine (0·825)	0·61–0·875	0·60–0·85
Semi-Diesel engines	25–27	Fuel oil (0·920)	0·63–0·69	0·55–0·60
Diesel type engines	30–33	Fuel oil (0·920)	0·45–0·50	0·39–0·43

At many large steam stations a coal consumption of less than 1·5 lb. per unit generated is common, but for a proper comparison with oil engines it must be remembered that Diesel sets are not at present installed in stations with a higher output than 10 million units per annum. The lowest coal consumption per unit in stations below this figure was 1·96 lb. per unit.

From the Annual Reports of the Diesel Engine Users' Association (1931–2) for forty stations the average oil consumption was 0·666 lb. per unit generated; 1932–3, for fifty-four stations it was 0·648 lb.

The largest Diesel engine constructed by 1934 was one of 22,500 H.P., having eight cylinders, and the following fuel consumptions are recorded for it: 0·35–0·36 lb. (14,000 to 20,000 H.P.); 0·4 lb. (8,000 H.P.); 0·48 lb. (5,000 H.P.).

Comparison Between Gas and Steam Plants. Discussion of the relative advantages of gas plants in comparison with steam plants for power production has lost much of its former importance. The recovery of ammonia in the larger plants is no longer a valuable offset to the cost of fuel, and, in the case of suction plants, the widely extended use of heavy oil engines for medium and small powers has reduced their importance. It will suffice therefore to make only a short comparison of gas plants with steam. With even the best boiler performances a gas producer shows a somewhat higher efficiency; it responds more readily to changing demands, and requires less upkeep. Producers show a better efficiency because for a given output they are smaller than boilers; there is less material to heat up and less loss by radiation. With suction plants and smaller pressure plants producers are simpler to operate, but larger-sized plants are regarded generally as requiring more attention and skill, and hence more difficult to work. This is due probably in a measure to the more general acquaintance with steam plants of the class of men available.

With a gas plant the transmission of the gas over comparatively long distances is a simple matter; there is no loss by condensation in pipes, and the pressures involved are but little above atmospheric, so that the pipe system is cheap as compared with steam piping. These considerations enable a central gas-generating plant to be arranged with distribution to engines over a wide area. The corresponding centralization with steam can be accomplished by electric distribution of power.

Diesel and Steam Plants. Very valuable comparisons of the cost of generating current in these two types of plant have been given by Tookey (*The Internal Combustion Eng.*, Nov., 1933, p. 3), who took units rated respectively at 100, 500, 1500 kW., and for each assumed an output of 66 per cent. of the rated full load. Each rating was further considered when working at one, two or three shifts per day. A summary of the data is given in Table LIX. In the total costs per unit generated all items, such as capital costs, interest, depreciation, etc., are included, and in the running costs, labour, lubrication, etc. It will be seen that with the larger plants there is but little difference in running costs or total costs on the basis of these figures, but a distinct advantage for the Diesel plants in the smaller rating.

TABLE LIX

COMPARISON OF STEAM AND DIESEL ENGINES

	Rated output .	100 kW.			500 kW.			1500 kW.		
	Shifts worked .	1	2	3	1	2	3	1	2	3
Steam.	Running costs, pence per unit .	0·93	0·90	0·89	0·42	0·42	0·42	0·35	0·31	0·30
	Total costs, pence .	1·325	1·15	1·09	0·715	0·60	0·57	0·59	0·46	0·42
Diesel.	Running costs, pence per unit .	0·61	0·64	0·62	0·42	0·38	0·36	0·34	0·31	0·30
	Total costs, pence .	0·99	0·87	0·80	0·69	0·55	0·50	0·55	0·44	0·41

GENERAL CONSIDERATIONS IN POWER PRODUCTION

The particular plant most suitable for power production under the very varying conditions in practice is often difficult to arrive at; indeed, as in most things, sharp lines of demarcation are frequently absent, and when all costs of installation, fuel charges and operating are taken into account, there is often little to choose between rival systems.

It is not within the scope of a book on fuel to discuss cost of plant, weight and space, which are important in the ratio they bear to fuel consumption and cost, but certain general considerations may be referred to briefly.

A very large proportion of the total fuel for power purposes is required in small plants, say, up to 100 H.P., and with such plants there is great latitude of choice. The small steam engine, especially if non-condensing, as is often the case, is notoriously inefficient, quite justifying its appellation of a " coal eater." This disadvantage at once places it so far behind the suction gas plant, gas engine on town supply, oil engine and, often, the electric motor, that it need be considered no longer as a competitor.

Where coal gas can be obtained at a reasonably low figure the question of its competition with suction-gas plant and oil engines is important. Coal gas offers certain advantages; there is a constant supply available of a fuel of very constant composition, the gas is perfectly clean, so that no water charges for purification are incurred, or attention to scrubbers, etc.; there are no stand-by costs, which for intermittent work is important, and the capital expenditure is limited in the case of gas to the engine, with sometimes the meter; with the oil engine to the engine and oil tank.

In districts not supplied with town gas the small consumer has the choice between suction gas and oil engines. For the usual small power rating of ordinary oil engines their cost, small space occupied, and ease of operation give them advantages which more than compensate for any higher fuel costs. The total number of Diesel engine sets has increased rapidly within the last few years, and they find application in the medium and small electric generating station, in water and sewage pumping and in many modern buildings for electric lighting sets.

Whilst low fuel consumption must be a factor of great importance in any power plant, it can be the deciding factor between different systems only when all costs, capital expenditure, depreciation, operating costs, etc., are all about equal. The advantages accruing to lower fuel consumption are in some cases more than counter-balanced by the lower fixed charges on some other system with somewhat higher fuel consumption. The consideration of all these contingent costs is clearly beyond the scope of this work; indeed, in nearly every case it depends *on such special factors that each requires careful individual consideration.*

One point which frequently is overlooked is that low fuel consumption involves, on the one hand, carrying less stock of fuel, with less capital expenditure in suitable stores, lower handling costs of the fuel and ashes, and frequently less loss by deterioration. On the other hand, where about the same stock is carried, the consumer is provided with far larger reserves of fuel for operating the plant when supplies may be interrupted through colliery strikes or transport difficulties.

APPENDIX

TABLE I

COMPOSITION, CUBIC FEET PER LB., WEIGHT OF 1 CUBIC FOOT AND CALORIFIC VALUE OF DRY GASES BURNT AT CONSTANT VOLUME

Gas.	Formula.	Weight per cu. ft. lb.		Cu. ft. per lb.		Calorific value in B.Th.U. per cu. ft.	
						At 0° C. and 760 mm.	At 60° F. and 30 in.
		At 0° C. and 760 m.m.	At 60° F. and 760 m.m.	At 0° C. and 30 ins.	At 60° F. and 30 ins.	Gross.	Gross.
Oxygen	O_2	0·0892	0·0846	11·22	11·82	—	—
Nitrogen	N_2	0·0785	0·0745	12·74	13·42	—	—
Air	—	0·0807	0·0766	12·39	13·05	—	—
Carbon dioxide	CO_2	0·1226	0·1163	8·15	8·60	—	—
Hydrogen	H_2	0·0056	0·0053	178·50	188·70	343·2	325·6
Carbon monoxide	CO	0·0780	0·0740	12·82	13·52	341·1	323·6
Methane	CH_4	0·0447	0·0424	22·38	23·58	1067·0	1012·0
Ethane	C_2H_6	0·0837	0·0794	11·95	12·59	1856·0	1761·0
Ethylene	C_2H_4	0·0781	0·0741	12·80	13·49	1673·0	1587·0
Propylene	C_3H_6	0·1171	0·1111	8·54	9·00	2467·0	2340·0
Acetylene	C_2H_2	0·0742	0·0704	13·48	14·20	1556·0	1476·0
Benzene	C_6H_6	0·2174	0·2063	4·60	4·85	4011·0	3805·0

TABLE II

WEIGHT AND VOLUME OF DRY OXYGEN AND AIR FOR COMBUSTION, INCLUDING WEIGHT OF PRODUCTS AND COMPOSITION OF FLUE GASES

Fuel. (dry).	Weight in lb.		Volume in cu. ft. per lb.				Volume in cu. ft. per cu. ft.		Products of combustion.					
	Per lb. fuel.		At 0° C. and 760 mm.		At 60° F. and 30 in.				Lb. per lb. of fuel.				Composition by vol. (Water condensed).	
	Oxygen.	Air.	Oxygen.	Air.	Oxygen.	Air.	Oxygen.	Air.	Total.	CO_2.	H_2O.	N_2.	CO_2.	N_2.
Hydrogen . .	7·94	34·24	89·1	424·3	93·9	447·3	0·5	2·38	35·24	—	8·96	26·28	—	100·0
Carbon (to CO_2) .	2·67	11·50	29·9	142·5	31·4	150·2	—	—	12·50	3·67	—	8·83	21·0	79·0
„ (to CO) .	1·33	5·73	14·9	71·0	15·7	74·9	—	—	6·73	2·33	—	4·40	34·7 (CO)	65·3
Carbon monoxide	0·57	2·46	6·4	30·5	6·7	32·1	0·5	2·38	3·46	1·57	—	1·89	34·7	65·3
Methane . . .	3·99	17·21	44·8	213·4	47·2	224·9	2·0	9·52	18·21	2·75	2·25	13·21	11·7	88·3
Ethylene . . .	3·43	14·78	38·5	183·4	40·6	193·3	3·0	14·28	15·78	3·14	1·29	11·35	15·0	85·0
Acetylene . . .	3·07	13·26	34·4	163·8	36·3	172·6	2·5	11·90	14·26	3·38	0·69	10·19	17·5	82·5
Benzene . . .	3·08	13·28	34·6	164·8	36·5	173·8	7·5	35·70	14·26	3·38	0·69	10·19	17·5	82·5

TABLE III

COMPOSITION AND PROPERTIES OF GASEOUS FUELS

Gas.	CO_2.	O_2.	CnHm.[1]	CO.	H_2.	C_nH_{2n+2}.	N_2.	S.G. air = 1.	B.Th.U. per cu. ft. sat. at 60° F.		Air for combustion.		Approx. vol. in cu ft. per lb. at 60° F. and 30 in. dry.	Theor. CO_2 of dry waste gases.
									Gross.	Net.	Theory.	Practice.		
Coal gas :														
Horizontal ret. . .	2·0	0·4	3·6	8·0	52·0	30·0 [2]	4·0	0·40	560	500	4·9	8·0	32·5	11·1
Continuous ret. . .	4·0	0·4	2·0	18·0	49·4	20·0 [3]	6·2	0·48	475	426	4·06	7·0	27·3	13·3
Water gas	4·7	—	—	41·0	49·0	0·8 [4]	4·5	0·54	295	270	2·22	4·0	24·3	20·6
Carburetted . . .	5·6	0·4	7·0	30·8	37·0	14·0 [5]	5·5 [1]	0·63	500	458	4·27	7·5	19·2	16·8
Producer gas :														
Coal	4·0	—	0·4	29·0	12·0	2·6	52·0	0·87	163	154	1·28	1·4	15·0	19·2
Coke	5·0	—	—	29·0	11·0	0·5	54·5	0·90	132	126	1·00	1·2	14·6	20·5
Air only	1·0	—	—	33·5	1·5	—	64·0	0·98	110	109 [2]	0·83	1·0	13·4	—
Blast-furnace gas . .	11·0	—	—	27·0	2·0	—	60·0	1·02	92	91	0·69	1·0	12·7	24·9

Assumed [1] $C_{2\cdot5}H_5$. [2] $C_{1\cdot07}H_{4\cdot14}$. [3] $C_{1\cdot12}H_{\cdot4\cdot24}$. [4] CH_4. [5] $C_{1\cdot1}H_{4\cdot2}$.

TABLE IV

WORLD'S OUTPUT OF CRUDE PETROLEUM IN THOUSANDS OF METRIC TONS

Countries.	1913.		1923.	1928.	1929:	1930.	1931.	1932.	1933.	
		Percentage of total.								Percentage of total.
BRITISH EMPIRE:										
Trinidad	84	0·16	424	1,067	1,210	1,308	1,353	1,406	1,328	0·67
India	1,115	2·15	1,181	1,229	1,229	1,249	1,225	1,239	1,229	0·62
Sarawak	20	0·04	580	751	760	707	529	340	327	0·17
Egypt	13	0·03	153	269	271	285	285	265	237	0·12
Canada	29	0·06	23	80	143	186	188	129	142	0·07
Total British Empire .	1,261	2·44	2,361	3,396	3,613	3,735	3,580	3,379	3,263	1·65
FOREIGN COUNTRIES:										
United States	33,126	64·02	97,654	123,592	138,104	123,117	116,683	107,556	123,133	62·16
U.S.S.R.	8,125	15·70	5,400	11,634	14,148	17,221	22,629	21,375	21,440	10·82
Venezuela	—	—	525	15,710	20,402	20,252	17,543	17,506	17,830	9·00
Rumania	1,885	3·64	1,510	4,282	4,837	5,744	6,658	7,337	7,376	3·72
Persia (Iran)	229	0·44	3,582	5,719	5,548	6,034	5,842	6,549	7,200	3·64
Mexico	3,835	7·41	21,440	7,598	6,733	5,914	4,935	4,896	5,234	2·64
Dutch East Indies . .	1,534	2·97	2,048	4,308	5,238	5,531	4,713	4,898	5,056	2·55
Argentina	19	0·04	535	1,323	1,365	1,301	1,697	1,892	2,022	1·02
Colombia	—	—	56	2,841	2,911	2,905	2,605	2,342	1,834	0·93
Peru.	248	0·48	751	1,591	1,777	1,656	1,345	1,320	1,826	0·92
Poland	1,087	2·10	725	743	743	675	663	631	557	0·28
Sakhalin	—	—	—	106	168	267	401	405	400	0·20
Germany	121	0·24	50	92	103	173	227	230	239	0·12
Ecuador	—	—	—	154	196	221	252	228	232	0·11
Japan and Formosa . .	259	0·50	252	270	281	271	273	230	202	0·10
Iraq	—	—	—	95	116	122	120	114	114	0·06
France	5	0·01	71	74	76	76	74	86	90	0·05
Italy	7	0·01	5	6	6	8	16	27	28	0·02
Czechoslovakia	—	—	11	14	14	23	20	19	17	0·01
Other Foreign Countries .	2	—	2	4	7	15	11	13	12	—
Total Foreign Countries	50,482	97·56	134,617	180,156	202,705	191,514	186,675	177,580	194,836	98·35
World's Total . .	51,743	100·00	136,978	183,552	206,318	195,249	190,255	180,959	198,099	100·00

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